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Environmental Monitoring Series

FATE OF HALOGENATED COMPOUNDS IN THE ATMOSPHERE

Interim Report – 1977

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Data suggest that the troposphere (northern hemisphere) contains 2906 ppt of chlorine atoms. The chlorine contribution of fluorocarbons is 33% of the total while that due exclusively to chlorocarbons is 77%. The natural chlorine contribution due solely to CH_3Cl is 25% of the total organic chlorine burden. The burden of halocarbons in the troposphere is increasing when compared to background data collected exactly a year ago.

Based on the budget and distribution of methyl chloroform and its emissions inventory, a two-box model was used to develop the conclusion that average tropospheric hydroxyl radical (OH) concentration was about 4×10^5 HO/ml. This is significantly lower than the hitherto accepted OH concentrations in the troposphere. It was further found that there may be significant gradients in the northern and southern hemispheric HO concentrations.

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ABSTRACT

The second year involved air monitoring at five sites that include urban, non-urban and marine. In situ analysis was performed for a total of 31 chemical species, nineteen were halogenated compounds, five were nitrogen containing species, and the remaining seven included hydrocarbon, CO, and O_3. Data suggest that the northern hemisphere troposphere contains 2906 ppt of chlorine atoms. The chlorine contribution of fluorocarbons is 33% of the total while that due exclusively to chlorocarbons is 77%. The natural chlorine contribution due solely to CH_3Cl is 25% of the total organic chlorine burden. The burden of halocarbons in the troposphere is increasing when compared to the background data collected exactly a year ago.

Based on the budget and distribution of methyl chloroform and its emissions inventory, a two-box model was used to develop the conclusion that average tropospheric hydroxyl radical (HO) concentration was about 4.1×10^5 HO/ml. This is significantly lower than the hitherto accepted HO concentrations in the troposphere. It was further found that there maybe significant gradients in the northern and southern hemispheric HO concentrations.

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INTRODUCTION

OVERVIEW

In this study, we attempt to characterize the concentrations, variabilities and distributions of a large number of halocarbons, hydrocarbons and other atmospheric trace constituents, which have a bearing on tropospheric/stratospheric chemistry. Many halocarbons stable in the troposphere (CCl_xF_y) are suspect as precursors of stratospheric ozone, destroying chlorine atoms while others are known for their toxicity and carcinogenicity. It is therefore essential that the urban-nonurban distributions of these species be determined.

The scope of the study in the second year was expanded to include a limited number of hydrocarbons, since it was felt that some of the nonmethane hydrocarbons may play an important role in the stratospheric chemistry of ozone. In addition, important tropospheric constituents that play an important role in the troposphere were included.

OVERALL OBJECTIVES

The overall objectives of this project are:

- To determine the distribution, atmospheric loading, sources, and sinks of halogenated compounds, selected photochemical pollutants, and natural trace constituents that have a possible stratospheric impact.
- To use halocarbons to understand complex atmospheric transport phenomena having a bearing on pollution control strategies.
- To use halocarbons as reactive tracers to understand natural tropospheric chemistry.

CONCLUSIONS

It is found that the atmosphere is contaminated with a large number of pollutants that disperse quite rapidly. While these pollutants are a source of great concern because of their ability to destroy stratospheric ozone, they also provide opportunities to better understand the natural atmosphere. The atmospheric burdens of species such as fluorocarbons (F11 and F12) are increasing at a rate comparable with their emissions. The atmospheric residence times calculated in this report lend credence to the contention that the stratosphere may be the only important sink for these species. Other chemical constituents such as methyl chloroform (and fluorocarbons 22) are scavenged at a slower rate than earlier believed and are also a source of great concern and cannot be allowed to be emitted at ever-increasing rates. A qualitative case for the control of carbon monoxide which reduces the scavenging ability of the atmosphere, can also be made.

SUMMARY

The second year results involved air monitoring at five urban and non-urban stations with the help of an instrumented environmental mobile laboratory. The monitoring stations included urban, remote marine, remote continental, high altitude and intermediate locations. In situ analysis was performed for a total of 31 chemical species and six meteorological parameters. Of the 31 chemical species sought, 19 were halogenated compounds. five were nitrogen containing species, and the remaining seven included hydrocarbons, CO and O_3.

Meteorological parameters measured were wind speed, wind direction, relative humidity, temperature, pressure and solar flux. The northern hemispheric background concentrations of the chemical species as measured at Point Arena, California (marine environment, cleanest site monitored; 38,57°N-123,44°W) in May 1977 are given in Table 1.

Table 1 data also suggest that the troposphere (northern hemisphere) contains 2906 ppt of chlorine atoms. The chlorine contribution of fluorocarbons is 33% of the total while that due exclusively to chlorocarbons is 77%. The natural chlorine contribution due solely to CH_3Cl is 25% of the total organic chlorine burden.

The burden of halocarbons in the troposphere is increasing. When compared to background data collected exactly a year ago (Singh et al., 1977) the following growth patterns are observed for the important halocarbons (see Table 2).

Atmospheric residence times of a number of important halocarbons have been calculated based on our measurements and the test available emissions data. These are summarized in Table 3.

The residence times of Fluorocarbon 12 and 11, as calculated from our data, are compatible with earlier assertions of no significant tropospheric sinks. The residence times of more reactive halocarbons were found to be

Table 1

BACKGROUND CONCENTRATIONS OF MEASURED TRACE CONSTITUENTS
IN THE NORTHERN HEMISPHERE
(Marine Environment)

Compound	Average Concentration (ppt)
Fluorocarbon-12	220.5 (19.8)††
Fluorocarbon-11	126.5 (12.4)
Fluorocarbon-22*	20-30
Fluorocarbon-21†	5.0 (1.9)
Fluorocarbon 113	22.6 (4.8)
Fluorocarbon 114	11.9 (5.2)
Sulfur hexafluoride	0.27 (0.03)
Carbon tetrachloride	123.6 (8.3)
Chloroform	19.9 (5.1)
Methylene chloride	44.8 (21.5)
Methyl chloride	733.3 (134.1)
Methyl iodide	4.8 (2.9)
Methyl bromide	20.1 (4.2)
Hexachloroethane	6.8 (1.4)
Methyl chloroform	110.7 (18.1)
Dibromoethane ‡	5.4 (1.0)
Tetrachloroethylene	33.4 (4.6)
Trichloroethylene	11.5 (1.0)
Phosgene	15.4 (4.2)
Nitrous oxide	314.9×10^3 (11.5×10^3)
Nitric oxides	$<5 \times 10^3$
Nitrogen dioxide	$<5 \times 10^3$
Peroxyacetyl nitrate (PAN) §	110.1 (55.3)
Peroxypropionyl nitrate (PPN) §	40.2 (16.5)
Ozone	35×10^3 (5×10^3)
Carbon monoxide	119×10^3 (14×10^3)
Total nonmethane hydrocarbons	--
Methane	1479×10^3 (19×10^3)
Acetylene	<400
Ethane	1932.6 (324.0)
Propane**	433.8 (163.7)

*Not quantifiable.

†Whether fluorocarbon 21 is a true atmospheric constituent or an experimental artifact still remains unresolved.

‡Dibromoethane was above 4 ppt only 39% of the time.

§PAN and PPN data are reported from the Reese River Site (No. 10) which was a clean Continental Site. No PAN and PPN data at Point Arena (Site 11) were obtained because of instrument breakdown.

**Propane was above 250 ppt only 15% of the time.

††Standard deviation.

Table 2

ATMOSPHERIC GROWTH RATES OF IMPORTANT HALOCARBONS

Compounds	Percent Increase in Tropospheric Budget over a One-Year Period (May 1976-May 1977)
Fluorocarbon-12	9
Fluorocarbon-11	11
Carbon tetrachloride	9
Methyl chloroform	12

Table 3

ATMOSPHERIC RESIDENCE TIMES
OF IMPORTANT HALOCARBONS

Compounds	Residence Time (years)
Fluorocarbon 12	50.0
Fluorocarbon 11	36.0
Methyl chloroform	8.0
Chloroform	1.7
Tetrachloroethylene	0.4

inconsistent with all prior estimates. These were significantly longer than believed.

Based on the budget and distribution of methyl chloroform and its emissions inventory, a two-box model was used to develop the conclusion that average tropospheric hydroxyl radical ($\overline{HO}$) concentration was about 4×10^5 HO/ml. This is significantly lower than the hitherto accepted HO concentrations in the troposphere. It was further found that there may be significant gradients in the northern and southern hemispheric HO concentrations. Within the limit of uncertainties, the average HO levels in the northern and southern hemispheres are defined by the following equations:

$$\frac{(\overline{HO})_{S.H.} + (\overline{HO})_{N.H.}}{2} = (\overline{HO})_{Globe} = 4.1 \times 10^5 \text{ HO/ml} \qquad (1)$$

$$\frac{(\overline{HO})_{S.H.}}{(\overline{HO})_{N.H.}} = 1.6 \text{ to } 3.0 \quad . \qquad (2)$$

It is inferred that the HO hemispheric gradient is caused by carbon monoxide (a principal sink for HO), which is present at a concentration of about 120 ppb in the northern hemisphere, compared to about 40 ppb in the southern hemisphere.

The finding of reduced natural HO levels and their depletion by carbon monoxide has three major consequences:

- Reactive halocarbons, such as methyl chloroform, have a long enough residence time to have a significant stratospheric impact if they continue to be emitted at their current exponential growth rates.
- Continued carbon monoxide emissions may further reduce the scavenging ability of the atmosphere resulting in even greater stratospheric intrusion of chlorinated hydrocarbons.
- Greater intrusion of nonmethane hydrocarbons into the stratosphere could alter the chlorine chemistry.

The most ubiquitous hydrocarbon other than methane is found to be ethane. The ground level flux of ethane has been estimated by us to be 5 to 10 million tons a year as compared to 200-400 million tons a year for CH_4.

Even though the stratospheric input of ethane is three orders of magnitude lower than methane, its reaction with chlorine atoms is three orders of magnitude faster. This could make ethane the second most important stratospheric hydrocarbon, which could provide a sink for Cl atoms, particularly in the lower stratosphere. To date methane is the only hydrocarbon that has been considered in stratospheric models.

Limited water samples from the Pacific Ocean (42°N-46°N) confirm the N_2O supersaturation in the Pacific. Extension of this limited data to the global oceanic environment suggests a marine N_2O source of 37 million tons a year. This corresponds to an N_2O residence time of 62 years. Atmospheric measurements of N_2O conducted over the last 20 months

indicate constant background with extremely small spatial and temporal variations.

The next phase of the second year research effort (Phase II) is planned currently to determine the global inventories of the pollutants of interest with special emphasis on the southern hemispheric burdens and the north/south distribution of trace constituents.

SECOND YEAR (PHASE I) PROGRESS

In this section we report progress accomplished subsequent to the first year research effort. The first year progress report has already been summarized (Singh et al., 1976). The following steps were involved:

- An SRI mobile laboratory was equipped and readied to measure a large number of air quality and meteorological parameters. These are listed in Table 4. A total of 19 halogenated and 12 nonhalogenated chemical species, along with important meteorological parameters, were measured. The inclusion of hydrocarbon analysis was prompted by our determinations of low HO levels in the troposphere and the possibility that the role of HCs in stratospheric chemistry may not be limited to CH_4.

- A total of five short-term monitoring studies with the help of the mobile laboratory were completed (Sites 7-11) Figure 1 shows the exact locations of these sites as well as the monitoring period. The locations were selected to be:
  - Clean marine
  - Clean continental
  - Clean high altitude
  - Urban contaminated.

The monitoring period spans through winter to early summer (May 1977). Sites 9 and 10 are clean air sites roughly 200 km and 500 km away from the nearest marine source, respectively. Both of these sites are mountain peak sites at elevations of 2379 m and 1982 m (MSL), respectively. Site 11 is a clean marine air surface site while Site 8 is an urban surface site (Riverside) in the south coast air basin. Site 7 at Mill Valley is an elevated marine site (762 m MSL) that can be strongly affected by urban transport from San Francisco.

- Site monitoring had the following features:
  - All field monitoring was conducted on a 24-hour daily schedule. Actual monitoring periods are shown in Figure 1.

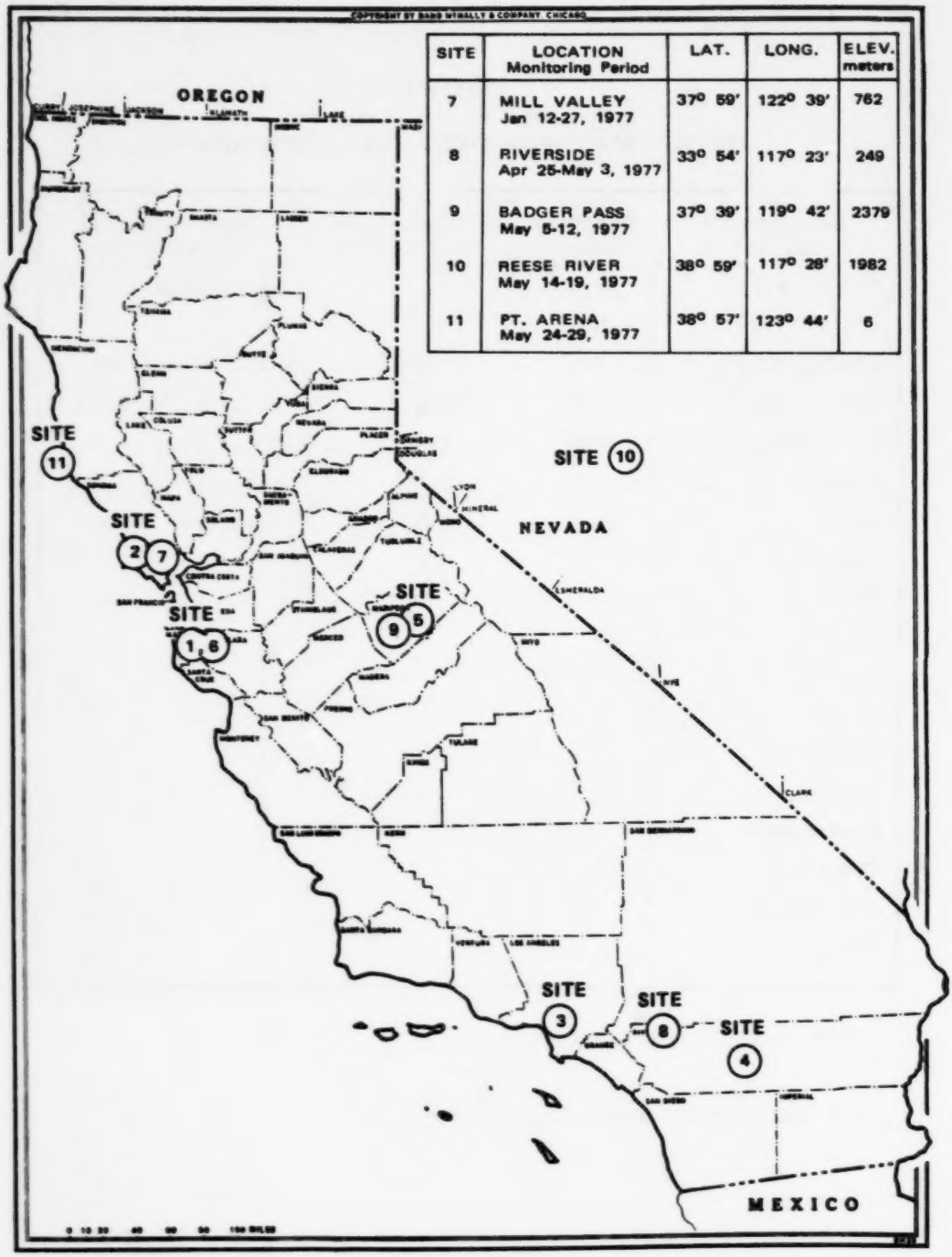
Table 4

CHEMICAL AND METEOROLOGICAL PARAMETERS MEASURED

Halogenated Species	Nitrogen Species	Hydrocarbons and Others	Meteorological Parameters
CCl_2F_2(F12)	N_2O	O_3	Wind speed
CCl_3F(F11)	NO	CO	
$CHClF_2$(F22)	NO_2	TNMHC*	Wind direction
$CHCl_2F$(F21)	PAN†	CH_4	Relative humidity
$CClF_2CCl_2F$(F113)	PPN†	C_2H_2	Solar flux
$CClF_2CClF_2$(F114)		C_2H_6	Temperature
SF_6		C_3H_8	Pressure
CCl_4			
$CHCl_3$			
CH_2Cl_2			
CH_3Cl			
CH_3Br			
CCl_3CCl_3			
CH_3CCl_3			
CH_2BrCH_2Br			
CCl_2CCl_2			
$CHClCHCl_2$			
$COCl_2$			

*TNMHC = Total hydrocarbons - CH_4

†PAN = $CH_3\overset{O}{\overset{\|}{C}}OONO_2$; PPN = $CH_3CH_2\overset{O}{\overset{\|}{C}}OONO_2$



SITE	LOCATION Monitoring Period	LAT.	LONG.	ELEV. meters
7	MILL VALLEY Jan 12-27, 1977	37° 59'	122° 39'	762
8	RIVERSIDE Apr 25-May 3, 1977	33° 54'	117° 23'	249
9	BADGER PASS May 5-12, 1977	37° 39'	119° 42'	2379
10	REESE RIVER May 14-19, 1977	38° 59'	117° 28'	1982
11	PT. ARENA May 24-29, 1977	38° 57'	123° 44'	6

FIGURE 1 LOCATION OF MONITORING SITES

- THC, CH_4, CO, NO_x, and O_3 were continuously monitored at all sites.
- Meteorological parameters (Table 4) were continuously monitored at all sites.
- Synoptic meteorological information was acquired separately.

- Table 5 shows the instrumentation in the SRI mobile laboratory. A stainless steel manifold was used to collect all air samples from a fixed elevation of 4 m above the ground.
- Extensive cryogenic concentrations of air samples were required at liquid oxygen temperatures to measure all hydrocarbons (except CH_4), F114, CH_3Br, CH_2Cl_2, C_2Cl_6, CH_2BrCH_2Br, C_2HCl_3, and SF_6. The collection volumes were generally less than 300 ml of air. As a general rule 200 ml of air were preconcentrated. In many cases cryogenically preconcentrated GC injections also provided data for species which could also be measured directly. Cryogenic concentrations were in stainless steel traps packed with glass wool. Materials were desorbed by rapidly heating the trap to 100°C for about 30 secs. In all cases a set procedure was followed for the cryogenic injections.
- Figures 2-10 show chromatograms of all species listed in Table 4 for which gas chromatographic analysis was used.
- Calibrations for halocarbons, hydrocarbons, PAN, PPN, N_2O and SF_6 were performed using permeation tubes, gas phase coulometry, and multiple dilutions as necessary. In addition, long term secondary standards were maintained and exchanged with other laboratories for intercomparisons. Several secondary standards were kept on board to ascertain the stability of instruments. In the case of PAN and PPN analysis, only gas phase coulometry was used and the data must be considered somewhat preliminary until the confirmations of the reliability of absolute PAN and PPN determinations using coulometry can be made. In the meanwhile, the data on PAN and PPN do look reasonable.
- Calibrations for THC, CO, and CH_4 were conducted on board at least twice a day. NO_2 calibrations were conducted using a permeation tube as primary standard. Standard secondary mixtures of NO and NO_2 were used in the field; O_3 primary calibrations were performed using the neutral buffer KI method and then monitored with the Bendix O_3 calibrator.

Table 5

AEROMETRIC INSTRUMENTATION IN SRI
ENVIRONMENTAL MOBILE LABORATORY

Component Measured	Instrumentation
Halocarbons, SF_6, and N_2O	Two Perkin Elmer 3920 GCs equipped with a total of four frequency-modulated EC detectors
	A coulometric EC detector with two detectors in series
CO, CH_4, THC	Beckman 6800 Air Quality GC
NO/NO_x^* (NO_2 by difference)	Bendix Model 8101-B chemiluminescence analyzer
O_3^*	Bendix Model 8002 chemiluminescence analyzer
Solar flux	Eppley UV pyranometer
Wind speed, wind direction, temperature, pressure, and relative humidity	Standard meteorological equipment
Data systems	Auto Lab System IV for the two Perkin Elmer GCs
	Digitem tape system for all other parameters

*A Teflon manifold was used for NO/NO_x and O_3 analysis; for all other measurements, a stainless steel manifold was used.

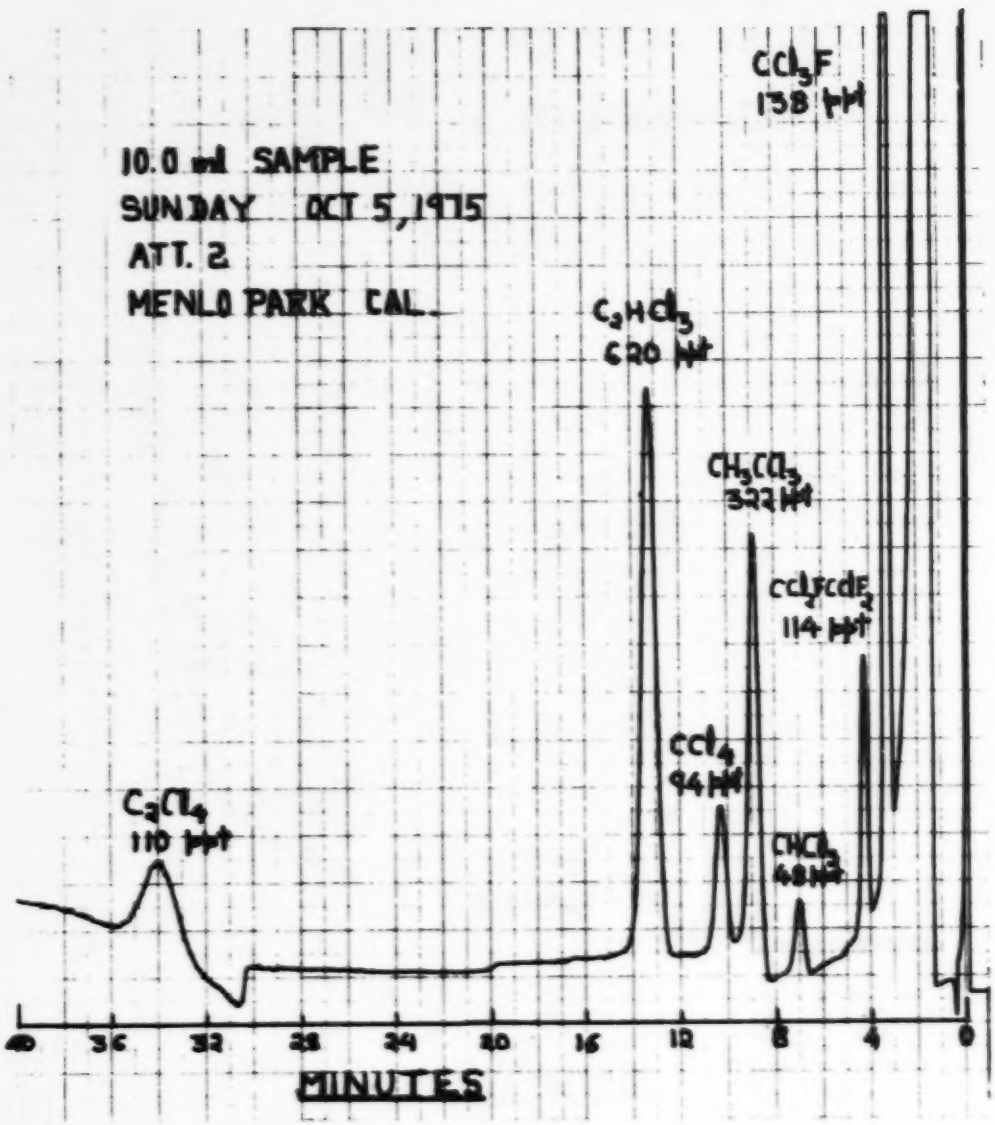


FIGURE 2 HALOCARBONS IN THE AMBIENT AIR AT MENLO PARK

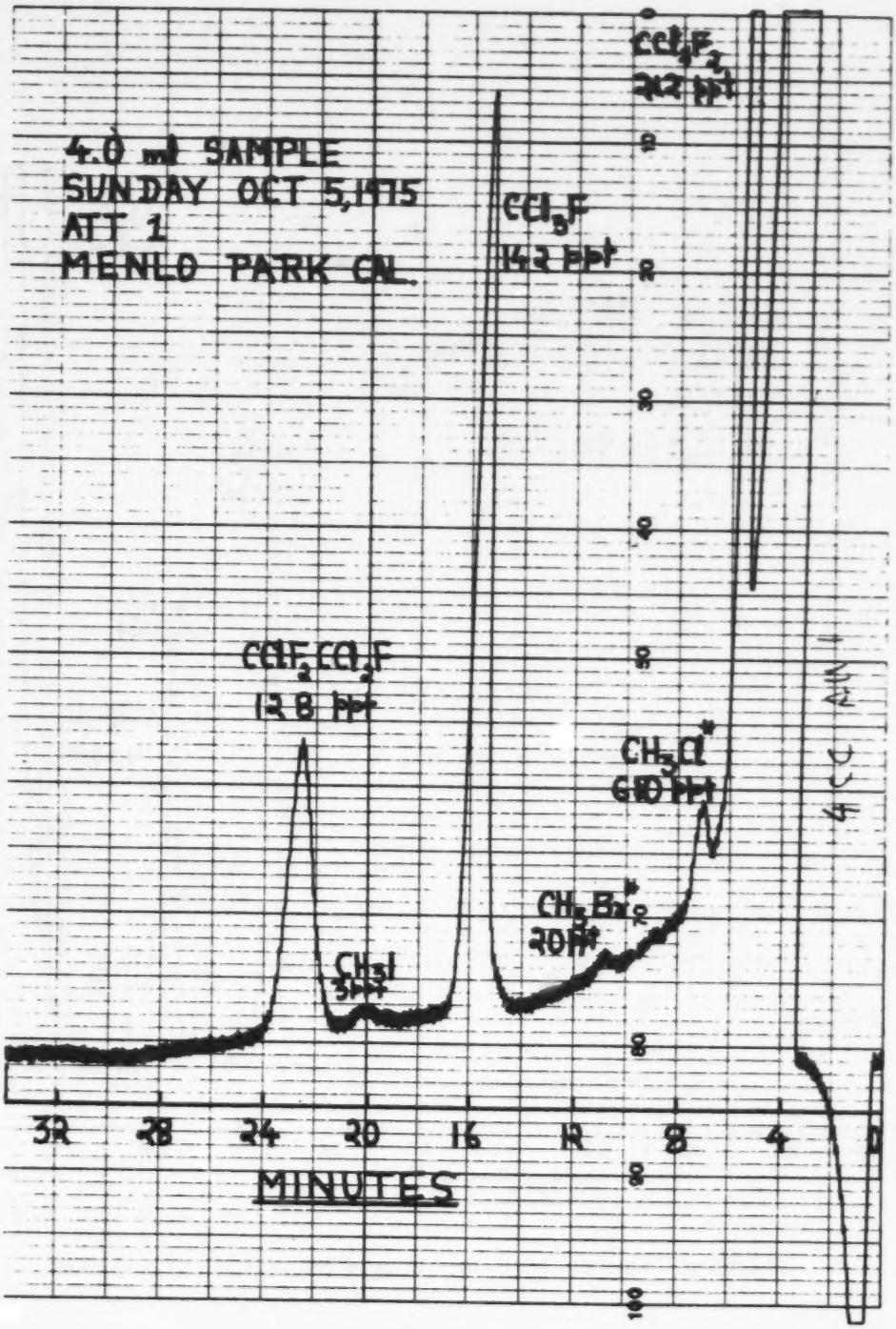


FIGURE 3 SEPARATION OF CH_3Cl, CH_3Br, AND CH_3I ALONG WITH OTHER HALOCARBONS

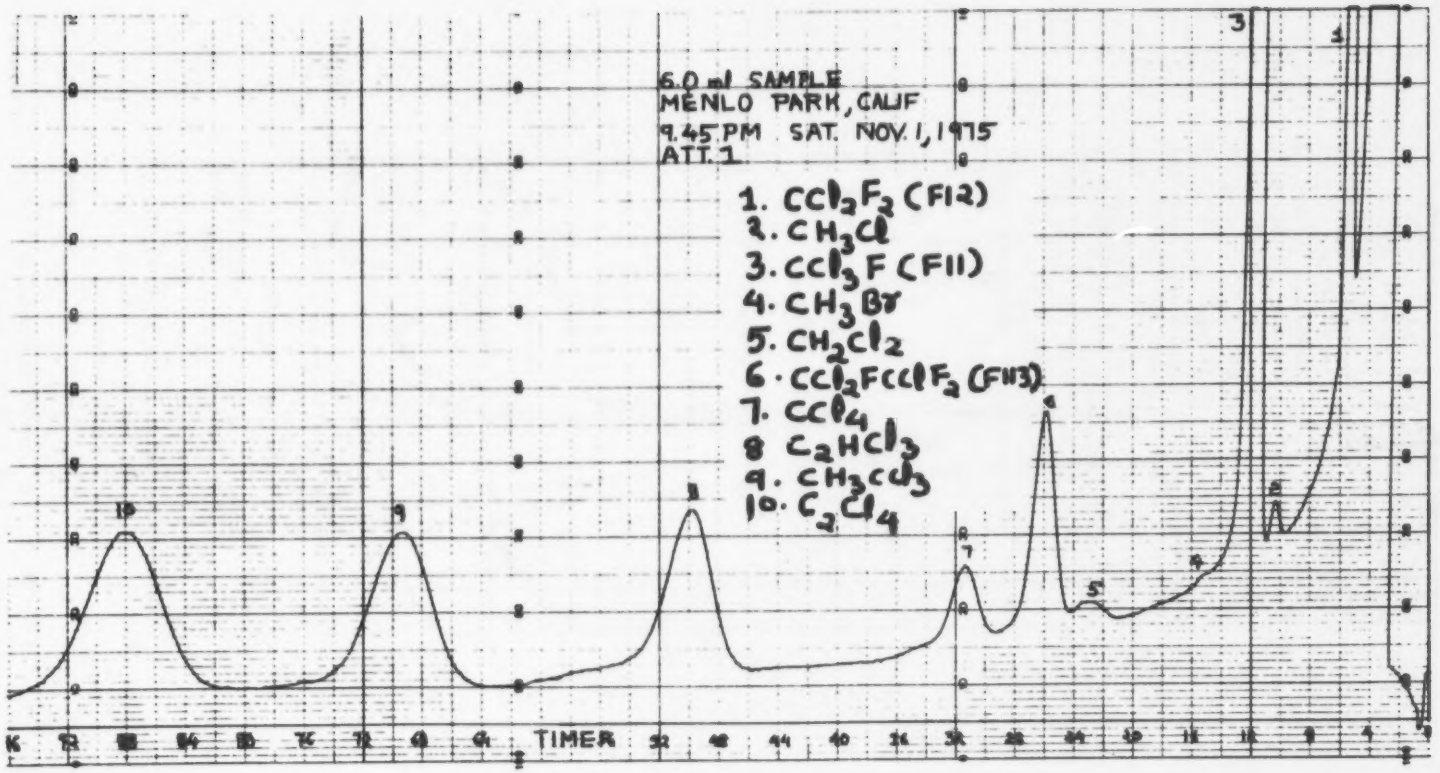


FIGURE 4 SEPARATION OF CH_3Cl, CH_2Cl_2 ALONG WITH SEVERAL OTHER HALOCARBONS

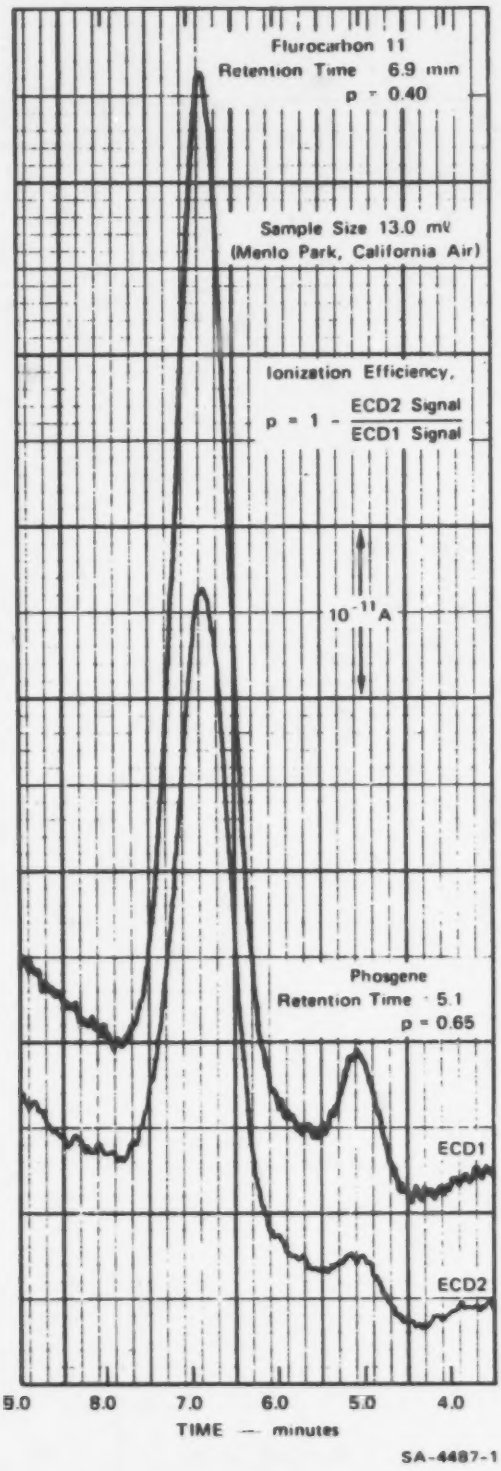


FIGURE 5 PHOSGENE SEPARATION FROM THE AMBIENT AIR

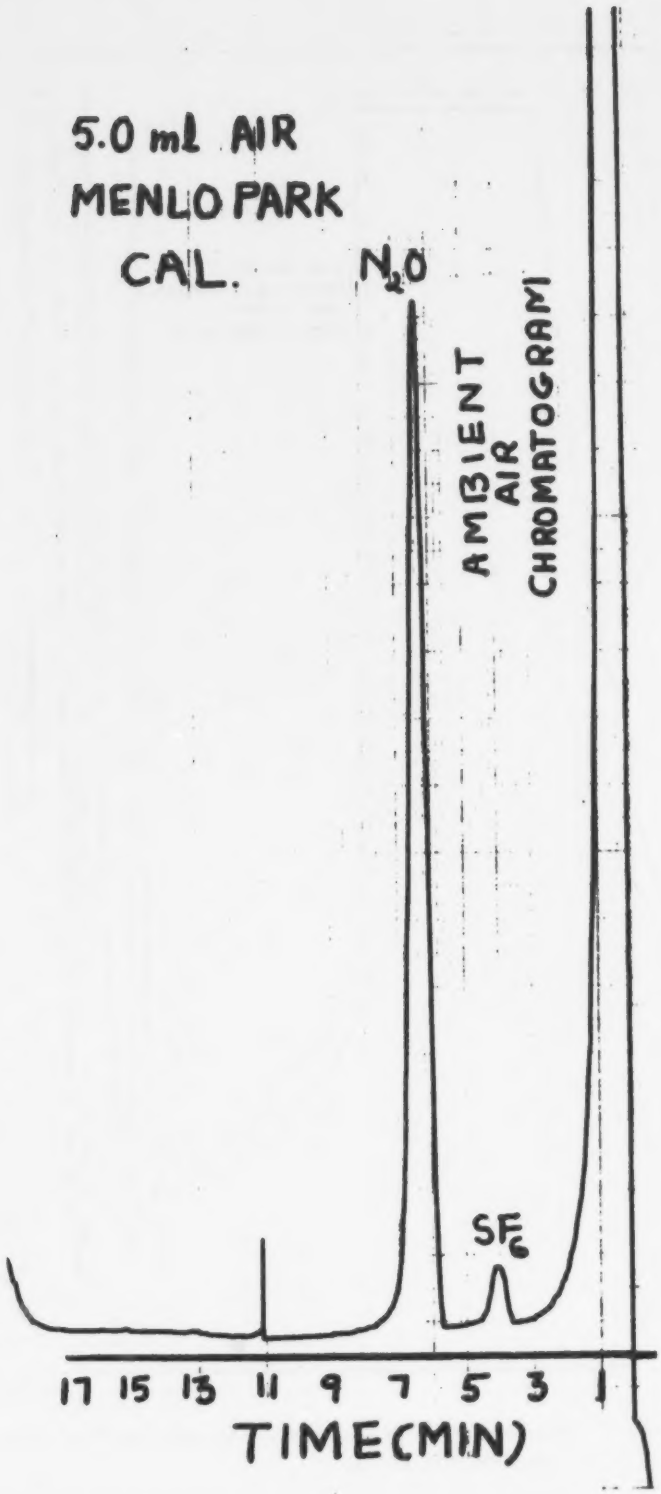


FIGURE 6 CHROMATOGRAM SHOWING SF_6 AND N_2O SEPARATION FROM AMBIENT AIR

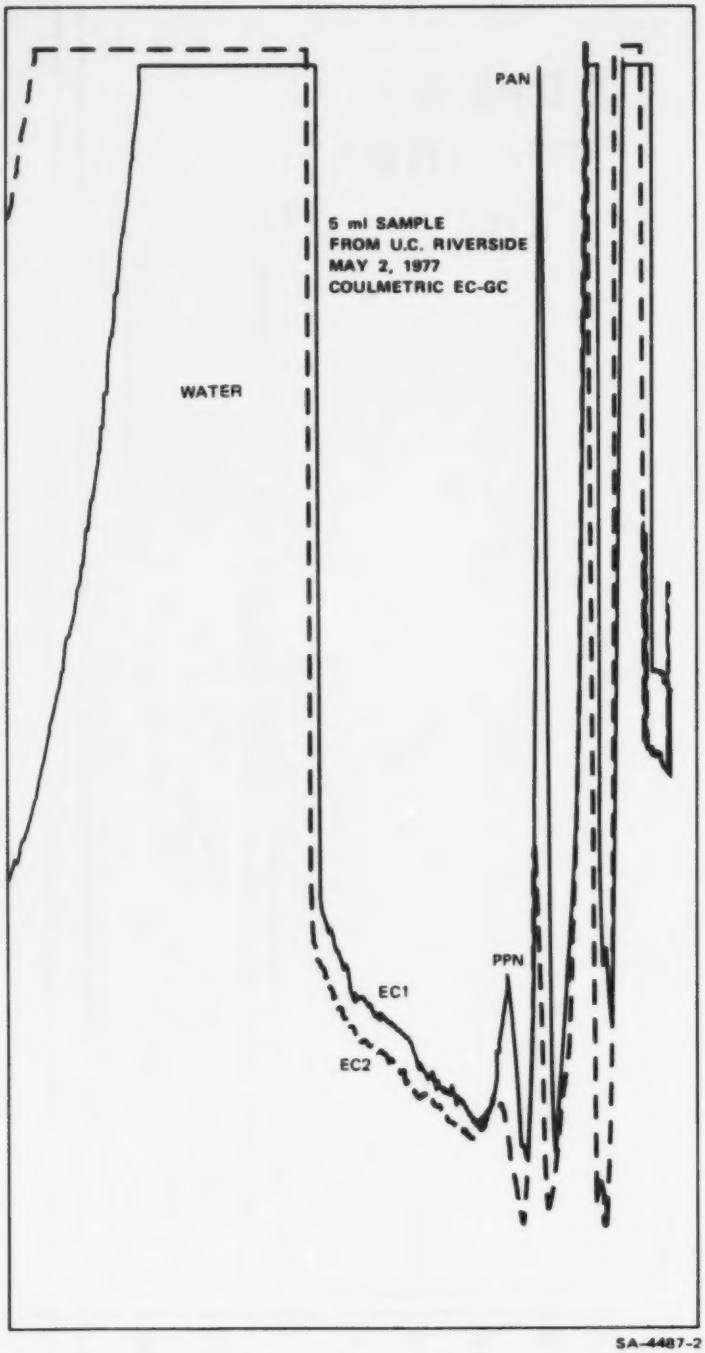


FIGURE 7 PAN AND PPN SEPARATION FROM AMBIENT AIR USING A COULOMETRIC EC-GC

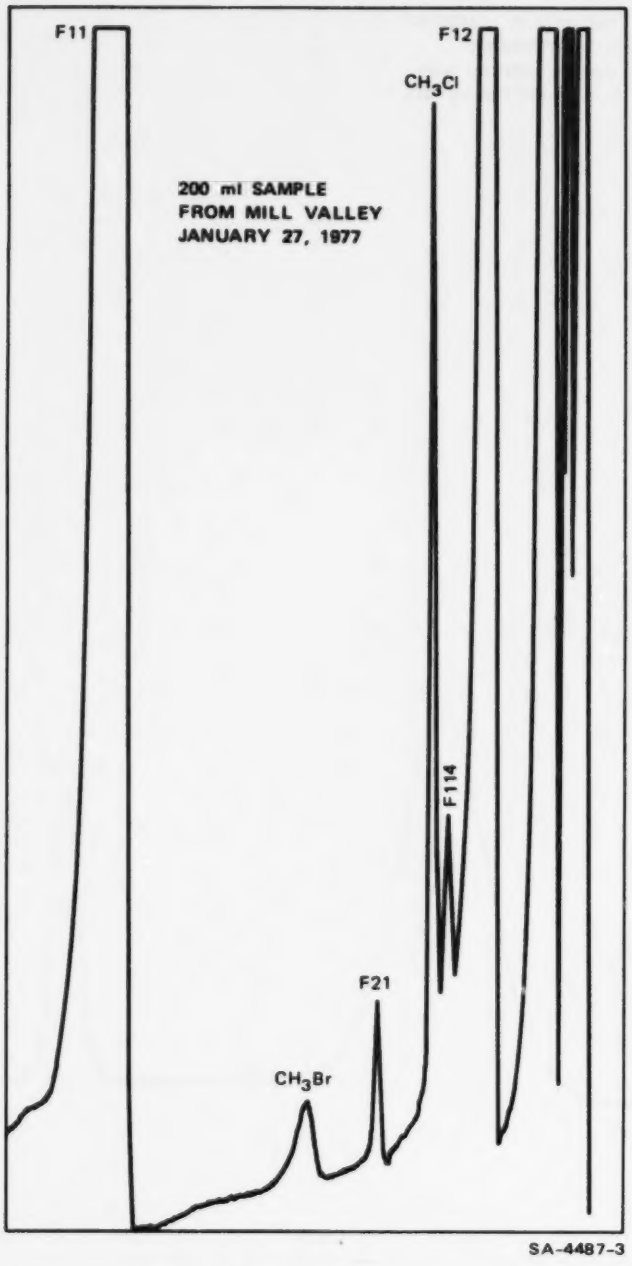


FIGURE 8 F114, F21 AND CH_3Br SEPARATION FROM AMBIENT AIR

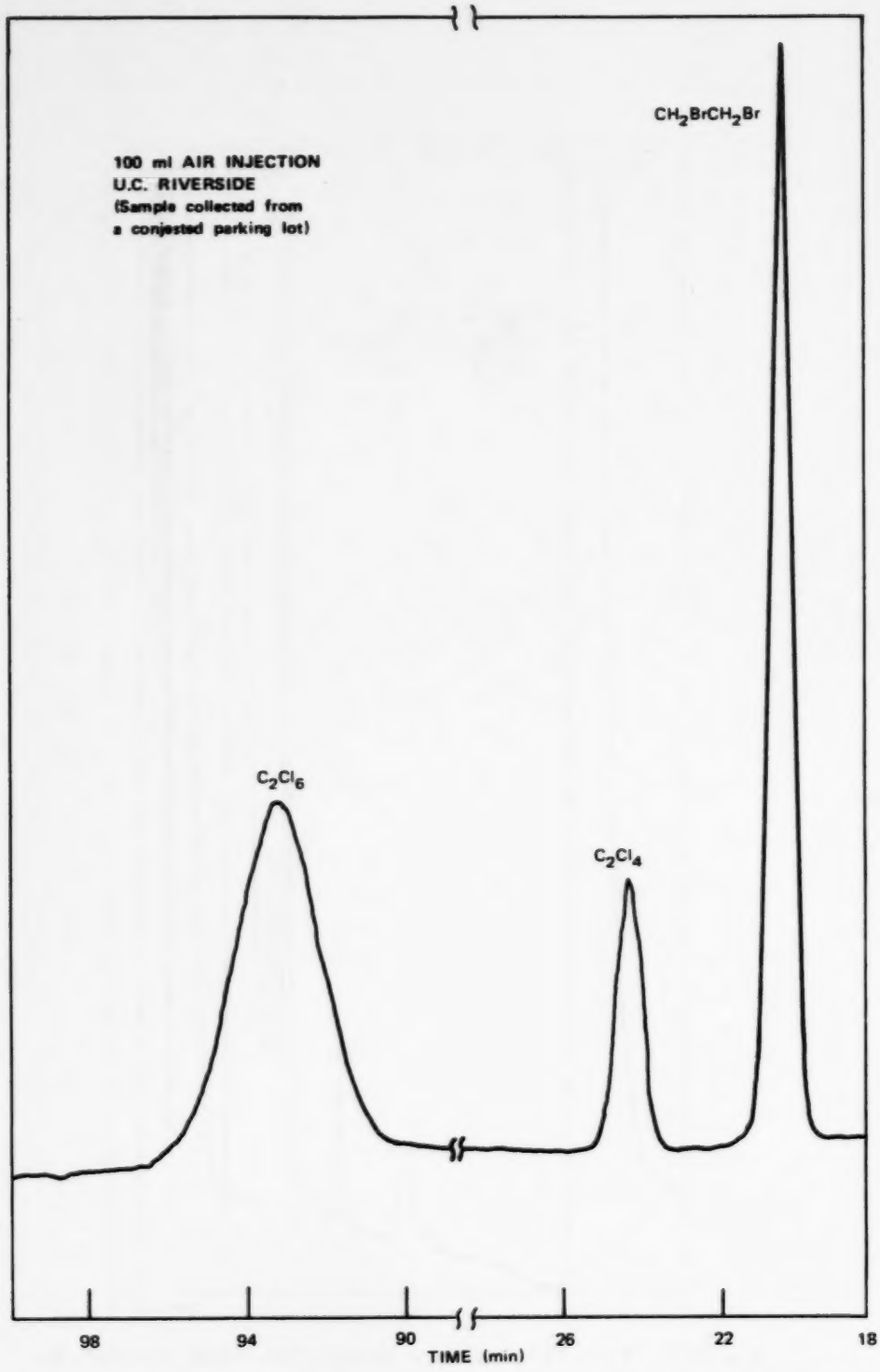


FIGURE 9 ETHYLENE DIBROMIDE AND C_2Cl_6 SEPARATION FROM AMBIENT AIR

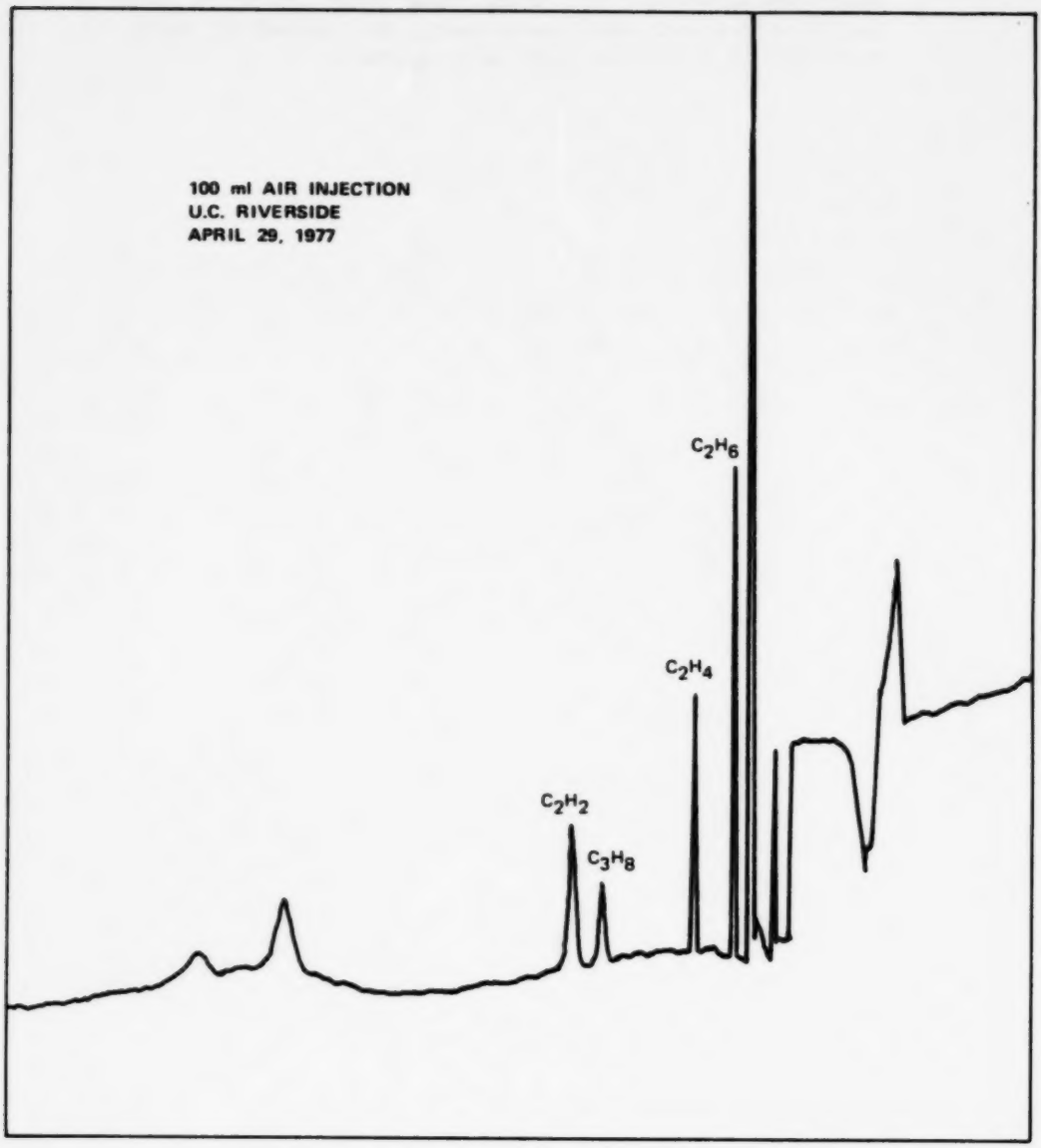


FIGURE 10 CHROMATOGRAM SHOWING LIGHT HYDROCARBON ANALYSIS

- A stainless steel manifold was used for all pollutant measurements except those for NO, NO_x, and O_3, for which a Teflon manifold was used. Stainless steel sampling loops were used for all GC injections. Concentrating procedures were developed and used successfully for ambient measurement. All GC-EC data were fed to an Auto Lab IV electronic data processor. All non-GC-EC data were fed to a Digitem tape data system.

DATA ANALYSIS

Experiments at all sites went satisfactorily and no insurmountable problems were encountered. The most difficult conditions were encountered at Badger Pass (Site 9) where we were caught in a snow storm. The higher standard deviations at Badger Pass are probably a reflection of the unfavorable weather conditions. Point Arena (Site 11) was found to be the cleanest site with consistent winds from the west-northwest. Riverside (Site 8) was representative of the urban site monitored by us. Because of our decision to monitor on a 24-hour daily basis, a vast amount of data was collected. Although all of the data have been treated statistically, our interpretation of the data is by no means complete. Nevertheless, we can provide a summary of preliminary observations. More detailed analysis and interpretations will appear in future reports and publications.

BACKGROUND CONCENTRATIONS OF MEASURED TRACE CONSTITUENTS

Table 6 shows a summary of data on the background concentrations of 19 halogenated and 11 nonhalogenated atmospheric trace constituents. The corresponding standard deviations are also shown. These are based on monitoring at Site 11, which was the cleanest site monitored. The winds were consistently from W-NW and the data is representative of background conditions. Table 6 also lists the background concentrations reported by us in May 1976 for comparison purposes.

Consistent with our earlier observations, all halocarbons (except CH_2BrCH_2Br) were found to be ubiquitous and could be measured within the sensitivities of our measurements 100% of the time. CH_2BrCH_2Br was detectable above 4 ppt at least 39% of the time. It is expected that the true background of concentration of CH_2BrCH_2Br is probably less than 4 ppt.

Seven fluorinated species (F12, F11, F22, F21, F113, F114, and SF_6) were sought and measured during the field programs. F12, F11, F113, F114,

Table 6

NORTHERN HEMISPHERIC BACKGROUND CONCENTRATIONS (ppt) OF TRACE CONSTITUENTS

Compounds	May 1976--Badger Pass (Lat. 37.40°N, Long. 119.39°W)		May 1977--Point Arena (Lat. 38.57°N, Long. 123.44°W)	
Fluorocarbon-12 (F12)	203.5**	(18.5)††	220.5	(19.8)
F11	115.6	(5.0)	126.5	(12.4)
F22	--		20 - 30*	
F21	14.2	(4.9)	5.0	(1.9)
F113	19.9	(3.4)	22.6	(4.8)
F114	--		11.9	(5.2)
SF_6	0.24	(0.04)	0.27	(0.03)
CCl_4	113.9	(6.5)	123.6	(8.3)
$CHCl_3$	17.1	(2.7)	19.9	(5.1)
CH_2Cl_2	--		44.8	(21.5)
CH_3Cl	713.0	(51.1)	733.3	(134.1)
CH_3I	9.2	(4.6)	4.8	(2.9)
CH_3Br	4.7	(2.6)	20.1	(4.2)
C_2Cl_6	--		6.8	(1.4)
CH_3CCl_3	98.8	(9.7)	110.7	(18.1)
CH_2BrCH_2Br	--		5.4	(1.0)†
C_2Cl_4	30.7	(10.5)	33.4	(4.6)
C_2HCl_3	15.6	(2.5)	11.5	(1.0)
$COCl_2$	21.7	(5.2)	15.4	(4.2)
N_2O	311.6×10^3	(18.2×10^3)	314.9×10^3	(11.5×10^3)
NO	< 5,000		< 5,000	
NO_2	< 5,000		< 5,000	
PAN	--		100.1	(55.3)‡
PPN	--		40.2	(16.5)‡
O_3	53×10^3	(12×10^3)	35×10^3	(5×10^3)
CO	--		119×10^3	(14×10^3)
CH_4	$1,412 \times 10^3$	(103×10^3)	$1,479 \times 10^3$	(19×10^3)
C_2H_2	--		< 400	
C_2H_6	--		1,932.6	(324.0)
C_3H_8	--		433.8	(163.7)§

Note: Concentrations of species such as CH_3Cl, CH_3Br are higher because of the marine environment of Point Arena.

* Not quantifiable.

† Measurable only 39% of the times above 4 ppt.

‡ PAN and PPN concentrations are taken from Reese River (Site 10), a clean continental site.

§ C_3H_8 was only detectable 15% of the times above 250 ppt.

** Average concentration in parts per trillion (10^{-12} v/v)

†† The quantity inside the parenthesis is the standard deviation.

and SF_6 background concentrations of 221, 127, 23, 12, and 0.3 ppt, respectively, are compatible with reported measurements by other investigators and our own earlier measurements. The ratio of F12/F11 of 1.74 compares well with a ratio of 1.76 reported earlier (Singh et al., 1976). The F113 concentration of 23 ppt is consistent with the concentration of 20 ppt and 21 ppt reported by Singh et al. (1976) and Dagmar et al. (1976) one year ago. Both F114 and SF_6 levels are generally compatible with the limited data available in literature. F21 could be measured all the time. It still remains uncertain, however, whether F21 is an experimental artifact or a true atmospheric constituent. F22 was observed but could not be quantified because of its poor electron capture response. A crude extrapolation will place its background concentration within 20 to 30 ppt.

Background concentrations of CCl_4, $CHCl_3$, CH_2Cl_2, CH_3Cl are measured to be 124, 20, 45, and 733, respectively. Once again, these concentrations are reasonable and not in disagreement with reported data. CH_2Cl_2 background of 45 ppt is being reported by us for the first time and comparative data is not available. Cox (1975), however, did report a CH_2Cl_2 concentration of 35 (±19) in 1974.

Concentration gradients of CH_3Cl, $CHCl_3$, CH_3I and CH_3Br between the marine and the continental environment were observed. Consistent with our earlier observations it still appears that CH_3Cl, CH_3I, and CH_3Br find a major source in the ocean. This may also be true for $CHCl_3$. However, most coastal areas are contaminated with $CHCl_3$ and a clear marine source relationship for $CHCl_3$ cannot be established at this time.

C_2Cl_6 has been measured for the first time in the ambient background atmosphere and is found to be a ubiquitous component. A background concentration of 7 ppt is observed. C_2Cl_6 is not manufactured in the United States, but about 500 tons a year are imported from Europe. Most of the C_2Cl_6 is released to the atmosphere eventually. It is also produced as an impurity during the manufacture of C_2Cl_4. It is likely that C_2Cl_6 abundance is a matter of long-time accumulation in the atmosphere. Natural sources of C_2Cl_6 may also exist. Additionally, chlorination of C_2Cl_4 can produce C_2Cl_6 in the absence of excess oxygen. C_2Cl_6 has been identified

in drinking water which has undergone chlorination. It is likely that stratosphere would be a major removal mechanism for C_2Cl_6. Tropospheric sinks are expected to be unimportant. We note here that C_2Cl_6 levels in Riverside (Site 8) were found to be significantly higher and a primary or a secondary urban source is indicated.

C_2Cl_4 and C_2HCl_3 were measured at 33 and 12 ppt, respectively. C_2HCl_3 background concentration of 12 ppt is somewhat lower than the 16 ppt reported earlier by us. However, in previous instances C_2HCl_3 was measurable at a frequency of less than 100%. Thus the latest concentration of 12 ppt for C_2HCl_3 reflects an improvement in the sensitivity of our measurements.

Phosgene is expected to be a photo-oxidation product of chloroethylenes (Singh, 1976) and was measured at a background concentration of 16 ppt.

N_2O was found to be distributed quite uniformly and was present at an average concentration of about 315 ppb. Figure 11 shows a plot of the average N_2O concentrations measured by us at several locations, based on short-term field measurements. It is clear from Figure 11 that no significant differences in N_2O levels over a period of 19 months can be deciphered. Thus N_2O levels are found to be relatively uniform in both space and time.

Oxides of nitrogen (NO, NO_2) were present at levels below the detection limit of our chemiluminescent instrumentation. It is safe to assume that these levels are below 5 ppb.

PAN and PPN were not measured at Point Arena because of instrument breakdown. However, at Reese River, a relatively clean continental site, concentrations of 110 ppt and 40 ppt for PAN and PPN were measured. These should be representative of the background conditions. Since PAN and PPN are photochemical products, significant seasonal variations can be expected.

Ozone was measured at a nearly constant concentration of 35 ppb. Maximum 1-h concentration did not exceed 46 ppb. The background of ozone at the surface is expected to show a significant seasonal and diurnal variation as suggested by Singh et al. (1977b).

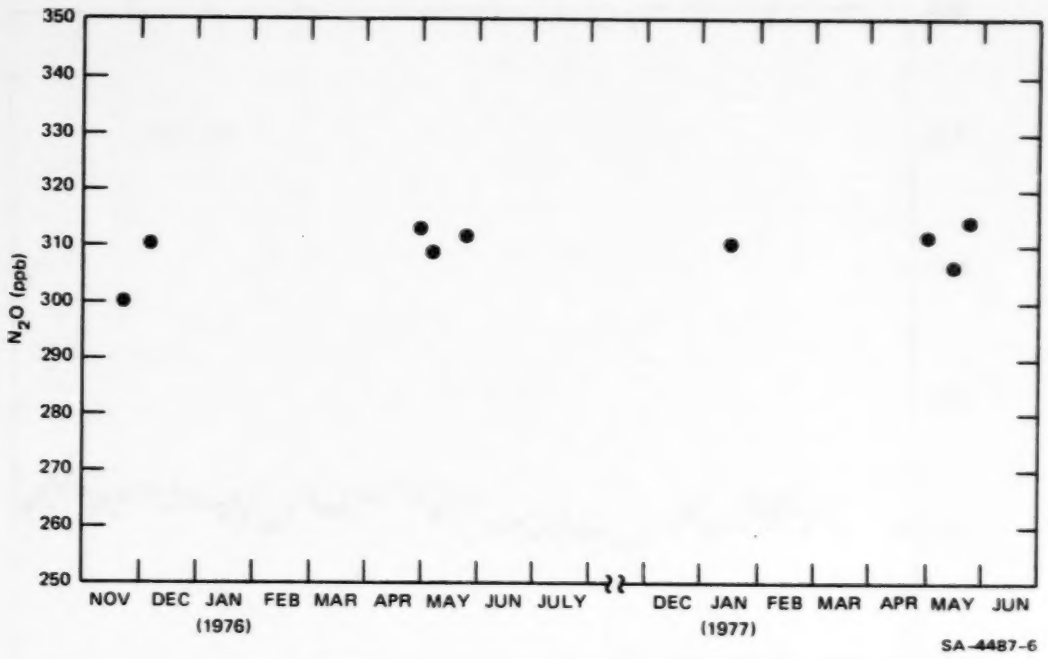


FIGURE 11 AVERAGE LONG-TERM N_2O VARIABILITIES IN THE TROPOSHERE

Carbon monoxide was measured at a nearly constant level of 119 ppb. This pacific marine air background concentration is identical to the CO levels of 117 ppb measured by Linnenbom et al. (1973) in 1970-1971. This implies that the background of CO has undergone no change at least since 1970. Figure 12 shows the relatively uniform background of CO at Site 11.

Methane was measured at a nearly constant level of 1480 ppb. This value is in good agreement with several other measurements although lower than the average 1600-ppb level reported by Heidt and Pallock (1976). No significant variations in the CH_4 concentration were observed (Figure 13).

Among the various C_2 hydrocarbons sought, C_2H_6 was found to be the most prevalent. A background concentration of 1930 ppb was measured at Point Arena. Figure 14 shows the atmospheric variabilities of C_2H_6 during the monitoring period at Point Arena (Site 11). The sources of C_2H_6 are not well known. Our best estimates suggest that if HO is the major

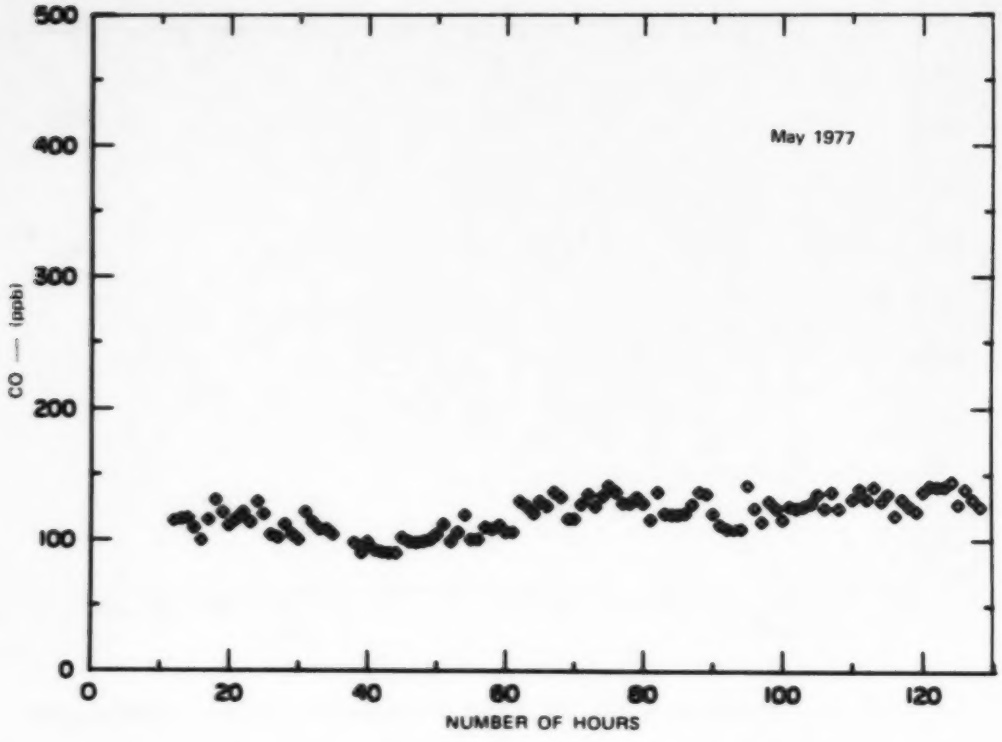


FIGURE 12 ATMOSPHERIC CO CONCENTRATIONS AT A CLEAN MARINE SITE (LATITUDE 38.9°N)

removal process for C_2H_6 in the atmosphere, its ground level flux must be of the order of 5 to 10 million tons a year. Similar calculations for CH_4 suggest a ground level flux of 200-400 million tons a year. We believe that even though the concentration of C_2H_6 in the atmosphere is about 10^3 times lower than CH_4 concentration, a distinct possibility exists that C_2H_6 plays an important role in the stratospheric chemistry. This is because the C_2H_6 + Cl rate constant is about 10^3 times faster than the CH_4 + Cl rate constant.

Hitherto, all hydrocarbons other than CH_4 have been considered to play an unimportant role in the stratosphere. It is suggested that C_2H_6 ought to be considered in the stratospheric models. The sources and sinks of C_2H_6 are still uncertain. However, our preliminary analysis of

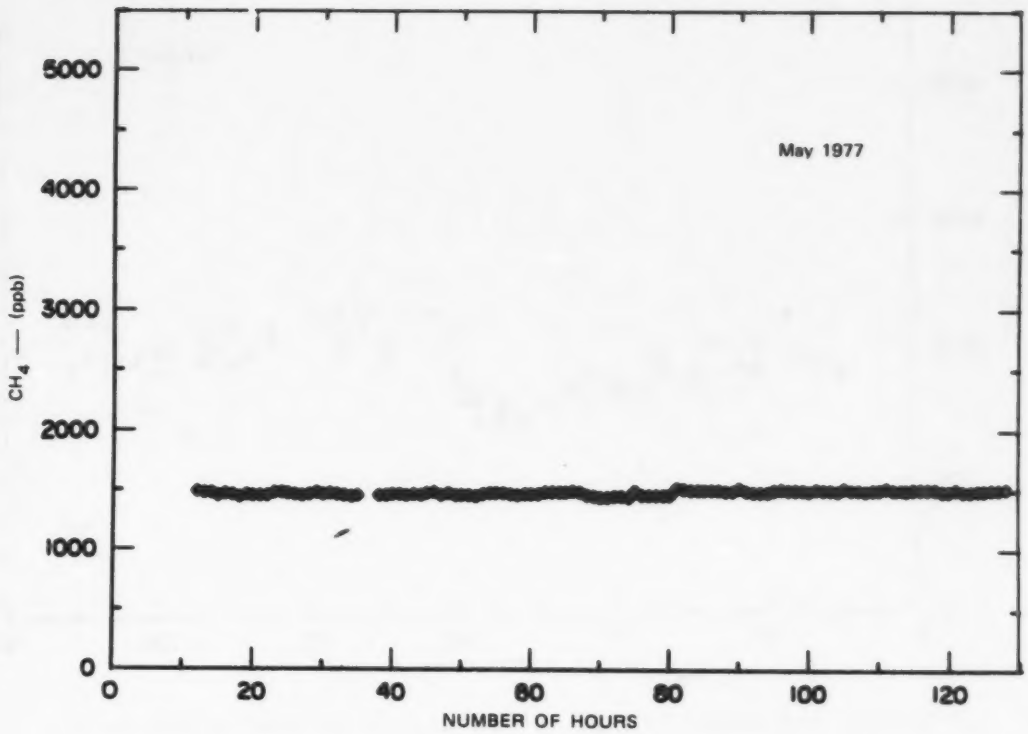


FIGURE 13 ATMOSPHERIC CH_4 CONCENTRATION AT A CLEAN MARINE SITE (LATITUDE 38.9°N)

emissions data from mobile sources suggests that mobile sources contribute no more than 20% of the atmospheric C_2H_6. Natural gas would be perhaps the most significant source of atmospheric C_2H_6. Other natural sources of C_2H_6 may exist also.

Acetylene and propane were also identifiable in the remote atmospheres, but these background concentrations were too low to quantify. It is expected that the true background concentrations of C_2H_2 and C_3H_8 are lower than 400 ppt and 250 ppt, respectively. While C_3H_8 was measured at 434 ppt at Point Arena, at least 85% of the time C_3H_8 was below our detectability limit of 250 ppt.

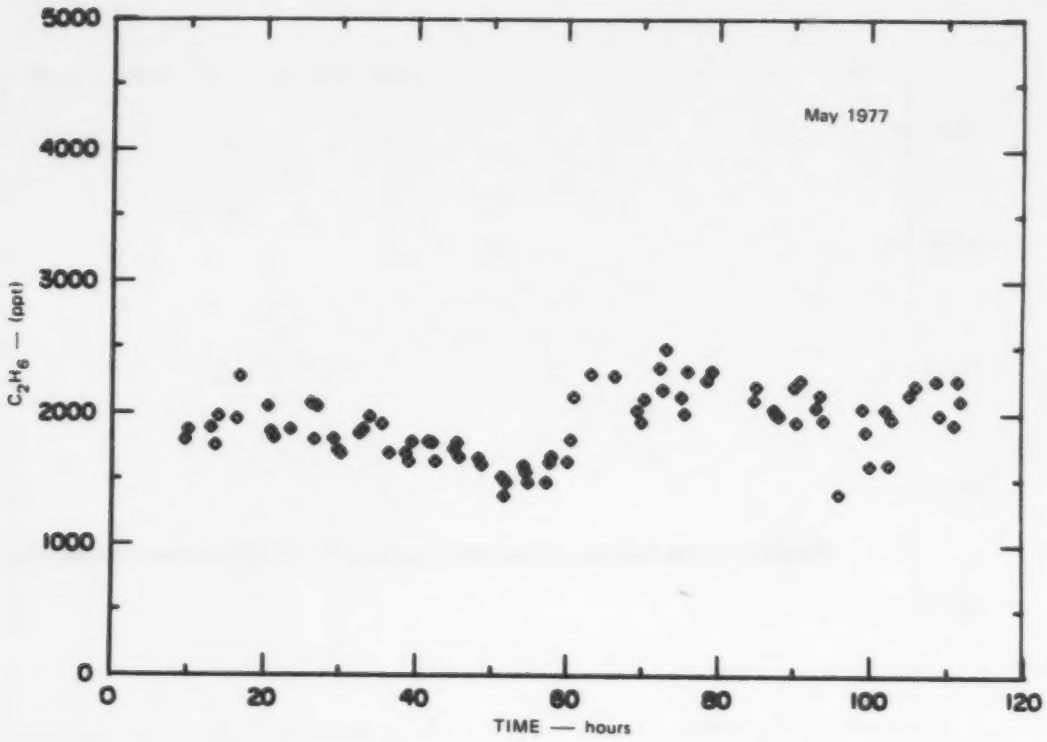


FIGURE 14 ATMOSPHERIC C_2H_6 CONCENTRATIONS AT A CLEAN MARINE SITE (LATITUDE 38.9°N)

The chlorine content of the northern hemispheric troposphere can be calculated to be 2906 ppt. The contributions due to fluorocarbons and chlorocarbons (nonfluorinated) were found to be 33% and 77% respectively. The natural chlorine contribution due to CH_3Cl alone was found to be about 25%. These proportions do not differ significantly from the 1976 proportions.

The northern hemisphere background of F12, F11, CH_3CCl_3 and CCl_4 increased at a yearly rate of 9, 11, 12, and 9 percent, respectively. While emissions of F12 and F11 have been changing in the United States, the growth rates do seem reasonable. The increase of 12% for CH_3CCl_3 is somewhat lower than expected, while the 9% increase for CCl_4 is higher than expected.

URBAN-NONURBAN POLLUTANT RELATIONSHIPS

Sites 7 through 11 were monitored both from the viewpoint of obtaining geochemical background levels, and also for generating urban-nonurban relationships. The carcinogenicity and toxicity of many halocarbons necessitate the determination of these relationships. Additionally, urban data is a good indicator of the anthropogenic source of several pollutants. These sources may be either primary or secondary.

Table 7 shows these relationships and provides a summary of data obtained during the five field studies. We emphasize that the reliability of Badger Pass (Site 9) may have been influenced by the very unfavorable weather conditions caused by snowstorms. Table 7 shows the minimum, maximum, and average concentration of pollutants at all sites. In addition, the standard derivations, number of data points, and the frequency of detection are provided. Site 11 (Point Arena) was the cleanest site monitored and should be most representative of background conditions. Site 10 (Reese River) was a relatively clean continental site and Site 8 (Riverside) is most representative of an urban environment.

Table 7 contains a great deal of data that is self-explanatory. While we defer more detailed discussions of the urban-nonurban relationships for future reports and publications, a few quick observations can be made:

- Maximum concentrations of F12 and F11 in urban areas remained below 4 ppb. The average concentration of F12 and F11 were less than five times their background levels.
- F21 was nearly always identified. Whether it is a true atmospheric constituent, or an experimental artifact, could not be conclusively established. At no time did the concentration of F21 exceed 23 ppt (Site 8); the average concentrations did not exceed 10 ppt.
- F113 and F114 could be measured at their maximum concentrations of 2.5 and 1.1 ppb, respectively. A clear urban source for F113 and F114 was indicated.
- The average concentration of SF_6 did not exceed 1 ppt at any of the sites monitored. At the urban site (Site 8), however, levels as high as 9 ppt were encountered.

Table 7

URBAN-NONURBAN POLLUTANT RELATIONSHIPS
(Concentrations of Atmospheric Trace Constituents)

Compounds (Concentration Units)	Mill Valley Site 7			UC Riverside Site 8			Badger Pass Site 9			Reese River Site 10			Point Arena Site 11		
CCl_2F_2 (ppt)	Max*	672.7	N** 121	Max	2,870.0	N 69	Max	476.1	N 55	Max	337.9	N 45	Max	272.2	N 47
	Min	214.1	f 1.0	Min	198.2	f 1.0	Min	191.8	f 1.0	Min	185.7	f 1.0	Min	179.8	f 1.0
	Av†	329.8 (106.0)‡		Av	503.9 (401.0)		Av	266.2 (29.3)		Av	239.4 (32.7)		Av	220.4 (19.8)	
CCl_3F (ppt)	Max	325.4	N 141	Max	3,300.0	N 93	Max	338.1	N 79	Max	233.5	N 34	Max	201.5	N 78
	Min	132.0	f 1.0	Min	122.1	f 1.0	Min	79.6	f 1.0	Min	117.6	f 1.0	Min	98.5	f 1.0
	Av	186.9 (32.2)		Av	505.5 (494.7)		Av	149.0 (41.6)		Av	144.7 (19.0)		Av	126.5 (12.4)	
$CHClF_2$ (ppt)	Max	30	N	Max		N	Max		N	Max		N	Max		N
	Min	20	f	Min	--	f	Min	--	f	Min	--	f	Min	--	f
	Av	--		Av			Av			Av			Av		
$CHCl_2F$ (ppt)	Max		N	Max	22.9	N 48	Max	12.4	N 45	Max	11.3	N 49	Max	8.3	N 42
	Min	--	f	Min	4.3	f 1.0	Min	0.3	f 1.0	Min	0.5	f 1.0	Min	0.4	f 1.0
	Av			Av	9.3 (2.9)		Av	8.1 (2.8)		Av	8.5 (2.1)		Av	5.0 (1.9)	
CCl_2FCClF_2 (ppt)	Max	180.7	N 261	Max	1,144.0	N 43	Max	255.0	N 120	Max	59.8	N 79	Max	41.7	N 34
	Min	13.0	f 1.0	Min	19.7	f 1.0	Min	13.1	f 1.0	Min	4.2	f 1.0	Min	14.2	f 1.0
	Av	40.8 (27.3)		Av	98.9 (166.0)		Av	26.5 (23.2)		Av	19.0 (7.1)		Av	22.6 (4.8)	
$CClF_2CClF_2$ (ppt)	Max	21.1	N 15	Max	212.3	N 17	Max	15.2	N 14	Max	15.4	N 28	Max	22.6	N 41
	Min	8.9	f 1.0	Min	6.4	f 1.0	Min	3.1	f 1.0	Min	3.0	f 1.0	Min	3.3	f 1.0
	Av	13.7 (4.0)		Av	52.7 (56.2)		Av	8.5 (3.5)		Av	9.4 (4.1)		Av	11.9 (5.2)	
SF_6 (ppt)	Max	0.46	N 7	Max	8.5	N 74	Max	1.60	N 44	Max	0.55	N 33	Max	0.34	N 32
	Min	0.34	f 1.0	Min	0.3	f 1.0	Min	0.19	f 1.0	Min	0.26	f 1.0	Min	0.16	f 1.0
	Av	0.39 (0.03)		Av	0.9 (1.4)		Av	0.40 (0.39)		Av	0.32 (0.06)		Av	0.27 (0.04)	
CCl_4 (ppt)	Max	185.8	N 153	Max	199.1	N 8	Max	226.4	N 58	Max	191.1	N 79	Max	142.6	N 72
	Min	101.8	f 1.0	Min	98.8	f 1.0	Min	86.6	f 1.0	Min	91.7	f 1.0	Min	106.0	f 1.0
	Av	131.9 (11.2)		Av	144.3 (30.5)		Av	124.5 (31.0)		Av	126.3 (18.8)		Av	123.6 (8.3)	
$CHCl_3$ (ppt)	Max	36.3	N 66	Max	310.0	N 12	Max	38.2	N 36	Max	19.1	N 29	Max	41.8	N 58
	Min	4.4	f 1.0	Min	24.0	f 1.0	Min	2.4	f 1.0	Min	5.9	f 1.0	Min	8.2	f 1.0
	Av	25.5 (5.3)		Av	67.0 (73.9)		Av	15.6 (8.1)		Av	12.7 (4.1)		Av	20.0 (5.1)	
CH_2Cl_2 (ppt)	Max	86.8	N 14	Max	473.4	N 20	Max	126.0	N 48	Max	98.7	N 24	Max	102.4	N 39
	Min	38.0	f 1.0	Min	33.1	f 1.0	Min	8.8	f 1.0	Min	14.7	f 1.0	Min	16.0	f 1.0
	Av	54.6 (14.5)		Av	110.6 (94.4)		Av	44.5 (25.0)		Av	51.5 (21.6)		Av	44.8 (21.5)	
CH_3Cl (ppt)	Max	1,319.5	N 136	Max	3,811.0	N 46	Max	1,522.1	N 33	Max	1,136.0	N 50	Max	1,212.8	N 39
	Min	391.5	f 1.0	Min	566.1	f 1.0	Min	313.1	f 1.0	Min	402.0	f 1.0	Min	497.7	f 1.0
	Av	730.3 (191.4)		Av	1,487.5 (731.8)		Av	724.9 (261.2)		Av	692.5 (177.6)		Av	733.4 (134.1)	
CH_3I (ppt)	Max	23.0	N 34	Max	25.7	N 36	Max	< 1	N 40	Max	< 1	N 34	Max	16.1	N 42
	Min	0.3	f 1.0	Min	1.0	f 1.0	Min	< 1	f 0.0	Min	< 1	f 0.0	Min	2.1	f 1.0
	Av	6.7 (6.5)		Av	10.4 (5.9)		Av	< 1		Av	< 1		Av	4.8 (2.9)	
CH_3Br (ppt)	Max	33.6	N 14	Max	176.6	N 26	Max	29.5	N 40	Max	10.1	N 34	Max	32.1	N 35
	Min	14.6	f 1.0	Min	7.4	f 1.0	Min	2.5	f 1.0	Min	2.4	f 1.0	Min	11.4	f 1.0
	Av	23.8 (6.0)		Av	45.5 (39.8)		Av	7.9 (6.1)		Av	5.2 (1.7)		Av	20.1 (4.2)	
C_2Cl_6 (ppt)	Max	12.0	N 22	Max	33.9	N 8	Max	10.6	N 13	Max	7.9	N 14	Max	8.6	N 28
	Min	4.0	f 1.0	Min	5.3	f 1.0	Min	1.9	f 1.0	Min	4.2	f 1.0	Min	3.2	f 1.0
	Av	5.9 (1.6)		Av	17.3 (9.8)		Av	6.2 (3.1)		Av	5.4 (0.9)		Av	6.8 (1.4)	
CH_3CCl_3 (ppt)	Max	894.6	N 109	Max	3,012.0	N 40	Max	341.6	N 51	Max	177.7	N 26	Max	150.3	N 36
	Min	107.1	f 1.0	Min	282.4	f 1.0	Min	130.3	f 1.0	Min	84.1	f 1.0	Min	82.6	f 1.0
	Av	312.6 (129.0)		Av	834.4 (560.3)		Av	229.2 (56.0)		Av	142.5 (21.9)		Av	110.7 (18.0)	
CH_2BrCH_2Br (ppt)	Max	22.8	N 11	Max	92.5	N 24	Max	< 4	N 13	Max	< 4	N	Max	6.5	N 28
	Min	5.2	f 1.0	Min	4.3	f 1.0	Min	< 4	f 0.0	Min	< 4	f	Min	4.0	f 0.39
	Av	10.5 (4.7)		Av	23.1 (18.6)		Av	< 4		Av	< 4		Av	5.4 (0.7)	

Table 7 (Concluded)

Compounds (Concentration Units)	Mill Valley Site 7			UC Riverside Site 8			Badger Pass Site 9			Reese River Site 10			Point Arena Site 11		
C_2Cl_4 (ppt)	Max	290.0	N 154	Max	2,325.0	N 19	Max	39.3	N 63	Max	38.8	N 48	Max	47.8	N 58
	Min	20.0	f 1.0	Min	96.0	f 1.0	Min	22.2	f 1.0	Min	22.4	f 1.0	Min	18.0	f 1.0
	Av	65.2 (48.9)		Av	983.2 (454.1)		Av	28.5 (4.6)		Av	31.8 (3.1)		Av	33.4 (4.8)	
C_2HCl_3 (ppt)	Max	90.2	N 56	Max	476.0	N 28	Max	15.7	N 20	Max	16.0	N 23	Max	12.4	N 15
	Min	9.4	f 1.0	Min	57.1	f 1.0	Min	10.4	f 1.0	Min	6.4	f 1.0	Min	10.1	f 1.0
	Av	26.0 (18.9)		Av	266.1 (93.6)		Av	12.5 (1.3)		Av	11.9 (2.4)		Av	11.5 (0.6)	
$COCl_2$ (ppt)	Max	36.0	N 100	Max	121.0	N 35	Max	19.8	N 11	Max	27.6	N 28	Max	23.7	N 21
	Min	5.8	f 1.0	Min	17.3	f 1.0	Min	7.8	f 1.0	Min	2.4	f 1.0	Min	9.2	f 1.0
	Av	17.9 (7.9)		Av	46.9 (20.6)		Av	13.1 (4.0)		Av	13.7 (7.3)		Av	15.5 (4.3)	
N_2O (ppb)	Max	355.8	N 93	Max	1,656.4	N 73	Max	487.3	N 31	Max	358.7	N 33	Max	337.9	N 31
	Min	276.0	f 1.0	Min	278.8	f 1.0	Min	265.8	f 1.0	Min	263.3	f 1.0	Min	297.3	f 1.0
	Av	309.8 (14.6)		Av	505.4 (285.6)		Av	315.3 (39.7)		Av	306.2 (22.3)		Av	314.8 (11.5)	
NO (ppb)	Max	22.5	N 213	Max	86.7	N 167	Max	2.8	N 153	Max	8.0	N 96	Max	5.5	N 117
	Min	0	f 0.98	Min	3.8	f 1.0	Min	0	f 0.32	Min	0	f 0.86	Min	0	f 0.35
	Av	9.0 (5.2)		Av	12.6 (12.4)		Av	1.2 (0.9)		Av	2.5 (1.5)		Av	2.2 (1.6)	
NO_2 (ppb)	Max	40.5	N 138	Max	60.5	N 167	Max			Max	1.2	N 96	Max	15.3	N 117
	Min	0	f 0.65	Min	3.5	f 1.0	Min	--		Min	0	f 0.40	Min	1.5	f 1.0
	Av	3.6 (5.2)		Av	27.3 (14.5)		Av			Av	0.5 (0.3)		Av	3.8 (2.2)	
PAN (ppt)	Max	868.0	N 77	Max	5,656.0	N 42	Max	238.0	N 7	Max	262.5	N 56	Max		N
	Min	84.7	f 1.0	Min	254.8	f 1.0	Min	47.6	f 1.0	Min	24.5	f 1.0	Min	--	f
	Av	311.4 (213.5)		Av	1,537.8 (1,475.4)		Av	139.0 (63.0)		Av	110.1 (55.3)		Av		
PPN (ppt)	Max	154.0	N 77	Max	1,820.0	N 44	Max	98.0	N 9	Max	87.5	N 41	Max		N
	Min	14.0	f 1.0	Min	70.0	f 1.0	Min	24.5	f 1.0	Min	17.5	f 1.0	Min		f
	Av	44.6 (28.4)		Av	320.1 (366.1)		Av	57.2 (23.3)		Av	40.2 (16.5)		Av		
O_3 (ppb)	Max	55.3	N 212	Max	123.7	N 165	Max	54.1	N 153	Max	55.6	N 96	Max	45.3	N 115
	Min	23.4	f 1.0	Min	0.2	f 1.0	Min	36.8	f 1.0	Min	10.3	f 1.0	Min	20.8	f 1.0
	Av	38.1 (5.8)		Av	37.2 (31.0)		Av	46.4 (3.0)		Av	38.3 (9.7)		Av	34.9 (5.3)	
CO (ppb)	Max	1,245.0	N 206	Max	2,597.3	N 167	Max			Max	328.0	N 88	Max	144.0	N 114
	Min	103.3	f 1.0	Min	142.7	f 1.0	Min	--		Min	108.0	f 1.0	Min	89.3	f 1.0
	Av	203.1 (113.7)		Av	766.2 (424.5)		Av			Av	147.8 (28.0)		Av	118.8 (13.8)	
CH_4 (ppb)	Max	1,760.0	N 206	Max	2,033.3	N 167	Max			Max	2,020.0	N 88	Max	1,513.3	N 115
	Min	1,400.0	f 1.0	Min	1,073.3	f 1.0	Min	--		Min	1,446.7	f 1.0	Min	1,440.0	f 1.0
	Av	1,458.8 (40.9)		Av	1,647.7 (150.4)		Av			Av	1,656.3 (157.3)		Av	1,479.2 (19.1)	
C_2H_2 (ppt)	Max	< 400	N	Max	9,063.0	N 45	Max	900.0	N 92	Max	< 400	N 73	Max	< 400	N 87
	Min	< 400	f	Min	627.0	f 1.0	Min	101.0	f 0.41	Min	< 400	f 0.0	Min	< 400	f 0.0
	Av	< 400		Av	4,469.2 (2,574.6)		Av	323.0 (170.2)		Av	< 400		Av	< 400	
C_2H_6 (ppt)	Max	3,602.2	N 15	Max	15,903.0	N 48	Max	7,581.0	N 92	Max	4,257.9	N 73	Max	2,503.5	N 87
	Min	1,278.2	f 1.0	Min	2,975.4	f 1.0	Min	1,197.0	f 1.0	Min	929.1	f 1.0	Min	1,368.0	f 1.0
	Av	2,039.7 (589.2)		Av	8,269.5 (3,708.6)		Av	2,990.5 (1,152.2)		Av	2,259.6 (506.6)		Av	1,923.7 (324.0)	
C_3H_8 (ppt)	Max	< 250	N	Max	10,108.0	N 14	Max	6,992.0	N 92	Max	1,140.0	N 73	Max	714.4	N 87
	Min	< 250	f	Min	3,173.0	f 1.0	Min	< 250	f 0.33	Min	< 250	f 0.40	Min	< 250	f 0.15
	Av	< 250		Av	5,951.1 (1,679.5)		Av	488.4 (1,215.5)		Av	295.1 (175.6)		Av	433.8 (163.7)	

Note: ppt = parts per trillion (10^{-12} v/v); ppb = parts per billion (10^{-9} v/v); ppm = parts per million (10^{-6} v/v).

* Maximum concentration.

* Minimum concentration.

* Average concentration.

* Standard deviation.

** Number of data points or number of hours for continuous instrumentation (NO, NO_2, O_3, CO, TNMHC, CH_4).

** Frequency of detection.

- Values of CCl_4 at Mill Valley (Site 7, downwind of San Francisco) and Riverside (Site 8) were found to be higher than at the clean background locations. This is consistent with our earlier view that CCl_4 is predominantly an anthropogenic pollutant and is still emitted in relatively significant quantities (Singh et al., 1976, Altshuller, 1976). Figure 15 clearly shows CCl_4 levels increasing with corresponding F11 levels based on the data taken by EPA in the northeast. Thus, the urban sources of CCl_4 are not limited to any special geographical regions. The maximum concentration of CCl_4 as measured by us did not exceed 0.3 ppb.

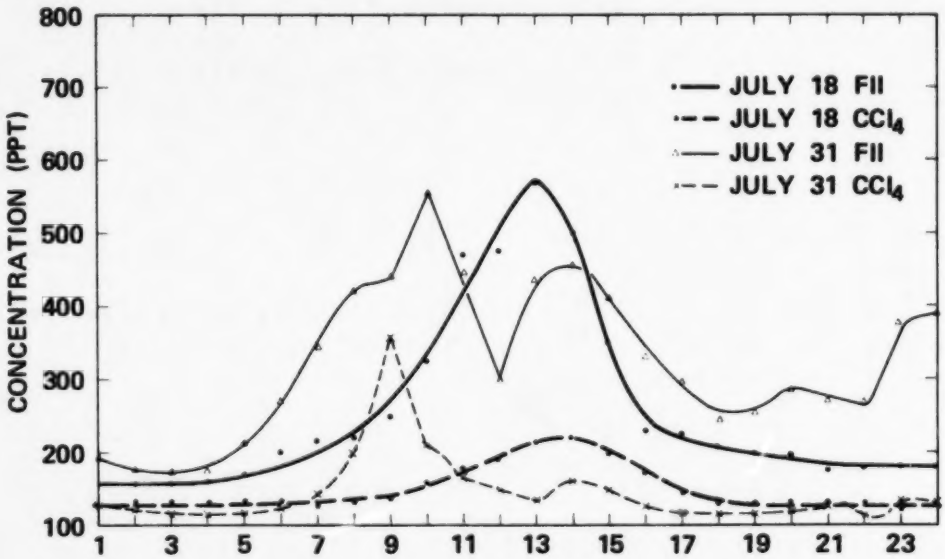


FIGURE 15 IDENTICAL CCl_3F AND CCl_4 BEHAVIOR AS AN INDICATOR OF A COMMON URBAN SOURCE IN THE EASTERN UNITED STATES

- Concentrations of $CHCl_3$ and CH_2Cl_2 did not exceed 0.5 ppb. It seems CH_3Cl finds significant usage, and at Site 8, CH_3Cl levels were found to be about twice the background levels.
- CH_3I has probably no anthropogenic sources, but CH_3Br levels up to 0.2 ppb indicate urban contamination. This is consistent with our first year findings when CH_3Br levels up to 210 ppt were measured in Los Angeles. The

average value of 46 ppt at Riverside can be compared with a concentration of 108 ppt measured by us in Los Angeles (Singh et al., 1976).

- C_2Cl_6 levels did not exceed 45 ppt at any of the sites monitored. The average concentration at Riverside, however, was about three times the background levels and an urban source is suggested.
- CH_3CCl_3 is a commonly used degreasing solvent and its concentration always remained below 3.1 ppb. Its average concentration of 0.8 ppb at Riverside is about eight times its background levels.
- CH_2BrCH_2Br was measured at concentrations not exceeding 0.1 ppb. The average urban concentration at Site 8, however, was about five times the expected background concentrations. This is consistent with an urban source of CH_2BrCH_2Br, which is known to be automobiles.
- C_2Cl_4 and C_2HCl_3 did not exceed concentrations of 2.5 and 0.5 ppb, respectively. The average urban levels of C_2Cl_4 and C_2Cl_3, however, were 30 and 22 times the background levels, respectively.
- Phosgene at levels somewhat higher than 0.1 ppb was measured. The urban levels (Site 8) were a factor of 3 higher than the background concentrations. The average $COCl_2$ concentrations at Riverside of 47 ppt was higher than the 1976 average value of 32 ppt measured in Los Angeles. This is probably because of the downwind nature of Site 8, which permits additional photooxidation of chloroethylene precursors.
- While N_2O was found to be distributed quite uniformly, urban levels as high as 1.6 ppm were measured. This is at variance with our earlier observations in Los Angeles where no significant N_2O intrusions were observed. Contamination from sources in the immediate vicinity is indicated.
- NO and NO_2 levels did not exceed 87 ppb and 61 ppb, respectively (Site 8).
- PAN and PPN levels did not exceed 6 ppb and 2 ppb, respectively. The average PAN/PPN ratio in Riverside was found to be about 5. In cleaner atmospheres, this ratio is reduced to about 2.5.
- O_3 levels did not exceed 125 ppb at any location monitored. At relatively clean locations the maximum 1-hour, O_3 valve was between 45 and 55 ppb. These levels suggest geographic uniformity of O_3 levels in clean atmospheres.
- CO levels up to 2.6 ppm (hourly average) were measured at Site 8.

- CH_4, C_2H_2, C_2H_6, and C_3H_8 maximum concentrations of 2.0 ppm, 9 ppb, 15 ppb, and 10 ppb, respectively, were measured. CH_4 levels in Riverside at least for some time dipped to 1.1 ppm, which is below the background level. No instrumental problems could be found. It is likely that a plume with CH_4 concentrations lower than the background passed over the area.

LIMITED OCEAN WATER ANALYSIS FOR N_2O

Ocean water samples from depths of 0, 50, 100, 150, 200, 250, and 300 m were obtained from the north Pacific. These samples were collected by the U.S. Coast Guard and analyzed at SRI for N_2O. A total of 28 samples were analyzed from two locations (41°35'N-125°55'W and 45°57'N-125°25'W). The corresponding water temperature was also available. The water samples were analyzed at 22°C and the N_2O concentrations were corrected then for temperature.

Figure 16 clearly shows the ocean denitrification zone below 100 m where N_2O is synthesized, and an average saturation approaching 325% was observed. The surface water supersaturation between these latitudes (42-46°N) was about 22%. Using a simplified film diffusion model and an average N_2O atmospheric concentration of 300 ppb, an average flux of 0.326×10^{-12} g/cm^2-s can be calculated. This compares favorably with estimates of Hahn of $0.22 - 0.47 \times 10^{-12}$ g/cm^2-s in the Pacific. Our flux estimate, if extended globally, results in an average N_2O flux of 37×10^{12} g/year from the marine sources.

It is possible to estimate the N_2O lifetime from this marine source alone. A flux of 37×10^{12} g/year and a uniform steady state N_2O concentration of 300 ppb correspond to a 62-year lifetime. Should additional sources of N_2O exist, the calculated lifetime will be lower than 62 years.

Additional data will be obtained during subsequent months of the second year effort to define the source capacity of the ocean for N_2O and some chlorinated species (e.g., CH_3Cl) more accurately.

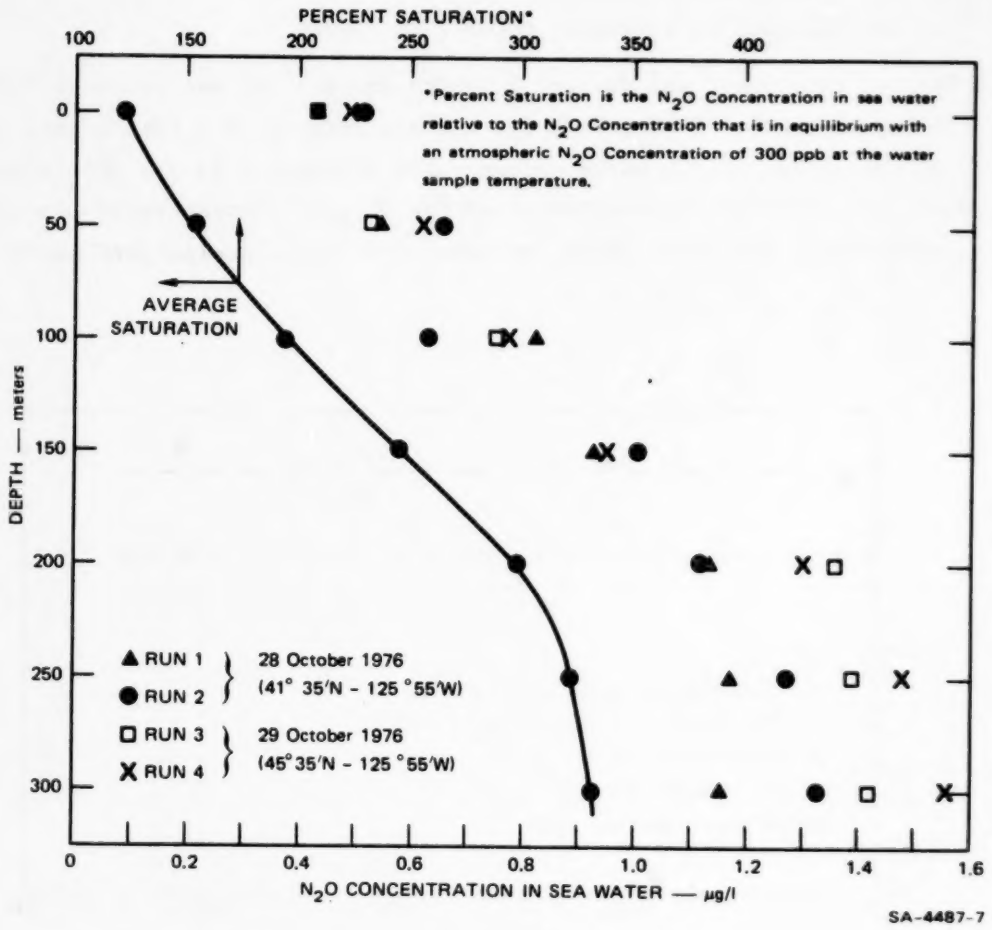


FIGURE 16 N_2O PROFILE IN THE PACIFIC OCEAN

PRELIMINARY TESTING FOR THE PRESENCE OF CHLOROACETYL CHLORIDES

The two major products of the photochemical oxidation of chloroethylenes are likely to be phosgene and chloroacetyl chlorides. While the former has been measured (Singh, 1976), methods for the measurement of low levels of chloroacetyl chlorides are not available currently. An indirect method therefore was employed to test for the existence of trichlororoacetyl chloride in the atmosphere. The method was based on two fundamental observations:

- A gas chromatographic column packing (DC-200) catalytically decomposed CCl_3COCl to CCl_4.
- CCl_3COCl is extremely soluble in water.

Thus an experiment was devised in which ambient air was passed continuously through a column of water and the air was analyzed for CCl_4 at the inlet and the outlet of the water column. The difference in the CCl_4 concentrations would be representative of the CCl_3COCl concentration in the atmosphere. Figure 17 shows the results of these preliminary experiments.

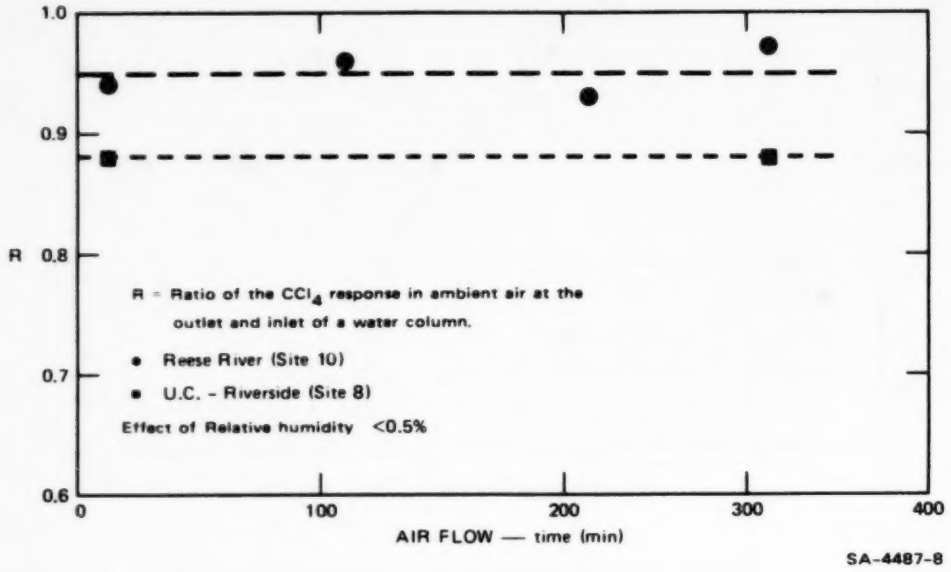


FIGURE 17 CCl_4 LOSS IN AMBIENT AIR WHEN PASSED THROUGH A COLUMN OF WATER

It was found that indeed the air emerging from the water column (100 ml of water; air flow rate = 250 ml/min) was deficient in CCl_4. This could mean two things:

- CCl_4 itself is lost to water and therefore may find a sink in rain-out processes.
- There are trichloroacetyl chlorides present in the air.

The fact that a greater loss of CCl_4 is observed at Riverside (Site 8) than at the cleaner Reese River location (Site 10) would tend to support the presence of CCl_3COCl at least in the urban environs. Indeed, both of the above possibilities may be true. Additional experiments are required to further refine these preliminary observations.

HALOCARBON LIFETIMES AND THEIR GLOBAL BALANCE

HALOCARBON LIFETIMES

Data were analyzed primarily to determine the lifetimes of halocarbons and to relate them to laboratory and modeling studies. In order to accomplish this, a tropospheric budget model was developed. The rate of increase of the pollutant mass in the atmosphere is given by

$$\frac{dM_i}{dt} = f_i(t) - \frac{M_i}{\tau_i} \tag{3}$$

where M_i is the accumulative mass in the troposphere of component i, $f_i(t)$ is input as a function of time of component i, and τ_i is the e-fold lifetime of component i. When $t = 0$, $M_i = 0$. (Note: The year 1920 is taken to be $t = 0$.)

The pattern of emissions for most halocarbons is best described by an exponential growth function. This choice is not arbitrary and is confirmed by emissions data:

$$f_i(t) = a_i \exp\left(b_i t\right) \tag{4}$$

$$\frac{dM_i}{dt} = a_i \exp\left(b_i t\right) - \frac{M_i}{\tau_i} \tag{5}$$

The above equation is easily solved,

$$M_i = \frac{a_i \tau_i}{b_i \tau_i + 1} \left[\exp\left(b_i t\right) - \exp\left(-t/\tau_i\right)\right] \tag{6}$$

$$R_i = \frac{\text{Amount present in the atmosphere at time } t_f}{\text{Amount actually added up to time } t_f} = \frac{M_i}{\int_o^{t_f} f_i(t)\, dt} \tag{7}$$

From Equations (4), (6), and (7), one can derive

$$R_i = \frac{b_i \tau_i}{b_i \tau_i + 1} \frac{\exp\left(b_i t_f\right) - \exp\left(-t_f/\tau_i\right)}{\exp\left(b_i t_f\right) - 1} \qquad (8)$$

For all compounds of interest here, $\exp(b_i t_f) \gg 1$ and

$$\exp\left\{-\left[b_i + \left(1/\tau_i\right)\right] t_f\right\} \ll 1 \quad .$$

Simplifying and rearranging equation (8),

$$\tau_i = \frac{R_i}{b_i\left(1 - R_i\right)} \qquad (9)$$

Equation (9) is always valid even if the atmosphere is significantly unmixed. The prime reason for deriving this budget model is that the fractional conversion of a first-order reaction is independent of initial concentrations, and therefore Equation (9) is independent of the mixing processes. This is an important consideration in the development of this model. For species such as CH_3CCl_3, it implies the use of a seasonally averaged HO concentration. For inert reactants such as F11 (F stands for fluorocarbon), it implies an overall empirical first-order loss and is not representative of a given mechanistic scheme. Equation (9) gives almost identical results for F11 when verified against the 1-D model of Rowland and Molina (1976). Table 8 shows the northern hemispheric background concentrations measured by us and the interhemispheric gradients as obtained from available data. Table 9 shows the detailed calculations of atmospheric residence times of several species.

The residence times of F12 and F11 (Table 10) are consistent with models that suggest no or insignificant tropospheric sinks. The longer lifetimes of tropospherically reactive species are inconsistent with the existing knowledge of atmospheric chemistry. Our conservative analysis of atmospheric halocarbon data shows that average HO concentrations must be 2 to 6 x 10^5 HO/ml instead of the accepted range of 10 to 30 x 10^5 HO/ml. These lower HO values tend to resolve the apparent discrepancies in the biospheric budgets and distribution of chlorinated hydrocarbons and CO.

Table 8

HALOCARBONS, SF_6, and N_2O
IN THE LOWER TROPOSPHERE

Compounds	Major Sources	Average Northern Hemispheric Background Concentrations,* ppt (10^{-12}v/v)	Ratio of Average Southern and Northern Hemispheric Concentrations[δ]
		Monitoring Period 5/12/76 - 5/17/76	
CCl_2F_2(F12)	A	203.5[†] (18.5)[‡]	0.89
CCl_3F(F11)	A	115.6 (5.0)	0.89
$CHCl_2F$(F21)**	A	14.2 (4.9)	--
CCl_2FCClF_2(F113)	A	19.9 (3.4)	--
SF_6	A	0.24 (0.04)	--
CCl_4	A	113.9 (6.5)	0.95
$CHCl_3$	A	17.1 (2.7)	<0.11
CH_3Cl	N	713.0 (51.1)	--
CH_3I	N	9.2 (4.6)	--
CH_3Br	N	4.7 (2.6)	--
CH_3CCl_3	A	98.8 (9.7)	0.42
CCl_2CCl_2	A	30.7 (10.5)	--
$CHClCCl_2$	A	15.6 (2.5)	0.10
$COCl_2$	SA	21.7 (5.2)	--
N_2O	N	311.6×10^3 (18.0×10^3)	1.00

N = Natural, A = Anthropogenic, SA = Secondary Anthropogenic

*Site Location: lat 37°39', long 119°40'; elevation 2360 m

†Mean of all data points collected

‡Standard deviation

δFrom Cox et al. (1976) and Rasmussen et al. (1976); also see text

**Preliminary data

Table 9

HALOCARBON RESIDENCE TIMES AND AVERAGE
HYDROXYL RADICAL CONCENTRATIONS

Compound	b_i (Years^{-1})	Emissions up to May 1976 in Million Tons (ppt)*	Measured Atmospheric Loading, May 1976, in Million Tons (ppt)	Fraction Present, $R_i \pm \Delta R_i$	Residence Time $T_i \pm \Delta T_i$ (Years)	Rate Constants with HO, k_{265} (265°K)		HO (10^5 molecules/ml)
						Davis (1976)	Kaufman (1976)	
F12	0.1230	4.6 (222)	3.9 ± 0.35+ (192 ± 17.4)	0.86 ± 0.08	50 ± 33	--	--	--
F11	0.1350	3.1 (131)	2.5 ± 0.11 (109 ± 4.7)	0.83 ± 0.03	36 ± 9	--	--	--
CH_3CCl_3**	0.1050	3.7 (162)	1.5 ± 0.15 (70 ± 6.9)	0.43 ± 0.04	7.2 ± 1.2	6.32×10^{-15}	1.28×10^{-14}	5.1(±0.9)‡ - 8.3(±0.6)§
$CHCl_3$**	0.1214	1.1 (52)	0.2 ± 0.03 (9 ± 1.4)	0.17 ± 0.03	1.7 ± 0.4	6.27×10^{-14}	9.28×10^{-14}	3.0(±0.7)‡ - 2.0(±0.5)§
C_2Cl_4	0.0970	11.7 (410)	0.5 ± 0.17 (16 ± 5.5)	0.04 ± 0.01	0.4 ± 0.2	--	--	--

*ppt is calculated by uniformly distributing the emissions in the troposphere

+standard deviation

‡from rate constants determined by Davis (from Chang and Wuebble, 1976)

§from rate constants determined by Kaufman (unpublished data, 1976)

**while emissions data for CH_3CCl_3 is quite accurate, $CHCl_3$ emissions may be in dispute

Table 10

RESIDENCE TIMES OF IMPORTANT HALOCARBONS

Compounds	Residence Times (years)
Fluorocarbon-12 (CCl_2F_2)	50.0 ± 33.0
Fluorocarbon-11 (CCl_3F)	36.0 ± 8.0
Methyl chloroform (CH_3CCl_3)	7.2 ± 1.2
Chloroform ($CHCl_3$)	1.7 ± 0.4
Tetrachloroethylene (C_2Cl_4)	0.4 ± 0.1

ESTIMATION OF HO RADICAL ABUNDANCE IN THE NORTHERN AND SOUTHERN HEMISPHERES

In the previous section we determined the average atmospheric residence times of several halocarbons. In this section, we shall concentrate on the global budget and hemispheric distribution of CH_3CCl_3 to determine the HO abundance in the northern hemisphere (N.H.) and the southern hemisphere (S.H.).

The uniqueness of CH_3CCl_3 as an indicator of HO abundance stems from two major considerations:

- Sources are entirely man-made and reliable emissions data are available.
- Reaction with HO is the major removal mechanism and the rate constant is accurately known (NASA, 1977), relatively fast, and not strongly dependent on temperature [$k = 3.5 \times 10^{12} \exp(-1562/T)$ ml/mol/s]; and CH_3CCl_3 is easy to measure and a relatively reliable global data base is available.

The average N.H. concentration of CH_3CCl_3 has been measured by several investigators (Singh et al., 1977; Cronn et al., 1976; Lovelock, 1977). Singh has reported an average lower tropospheric concentration in May 1976 of 99 ppt (10^{-12} v/v) based on all of the data and a concentration of 91 ppt based on the lower 50% of the data. Cronn has conducted

aircraft measurements at several altitudes within the troposphere and reported an average tropospheric concentration of 95 ppt. A 5% to 10% vertical concentration gradient at the surface and near tropopause altitudes was also observed. Lovelock has reported a N.H. concentration of about 90 ppt in early 1976. Thus, the N.H. CH_3CCl_3 background concentration ranges from 89 to 90 ppt in May 1976. Because of some vertical gradients, the true background of CH_3CCl_3 is probably closer to 90 ppt. In our present calculations, a lower and upper range of 89 and 99 ppt were considered. Subsequent calculations will be based on a N.H. background concentration of 89 ppt, unless otherwise stated. We may add that the case for reduced HO levels, as well as for a larger HO gradient between the N.H. and the S.H., is made even more strongly if one considers the upper limit of the background concentration (99 ppt in May 1976). The use of 89 ppt (lower limit), in our opinion, is both more reliable and also conservative.

The S.H. data are limited but a north/south concentration ratio of 1.43 has been reported by Rasmussen (1976) from S.H. data collected in New Zealand and at the South Pole. This is at variance with the data reported by Lovelock (1977), who reports a north/south ratio of about 2. Because of the consistent use of internal standards and reliable intercalibrations with our data, we believe that Rasmussen's data for the southern hemisphere are probably reliable. Also, we find that the growth of atmospheric CH_3CCl_3, as reported by Lovelock, is more rapid than the emissions data would allow. Hence we shall consider the data reported by Rasmussen for the present study but add that a larger ratio, as reported by Lovelock, only enhances the HO differences between the two hemispheres. The calculations reported here are therefore kept conservative by considering a north/south ratio of 1.43 to 1.53.

The growth of CH_3CCl_3 emissions has been nearly exponential since at least 1957. Figure 18 shows the most recent global emission inventory of CH_3CCl_3 since 1951 (private communication of J. Plonka--Dow Chemicals). The growth prior to 1957 does not fit the prescribed exponential pattern, but the errors due to this deviation are minimal since both simulated and actual emissions prior to 1957 are less than 3% of the total emissions.

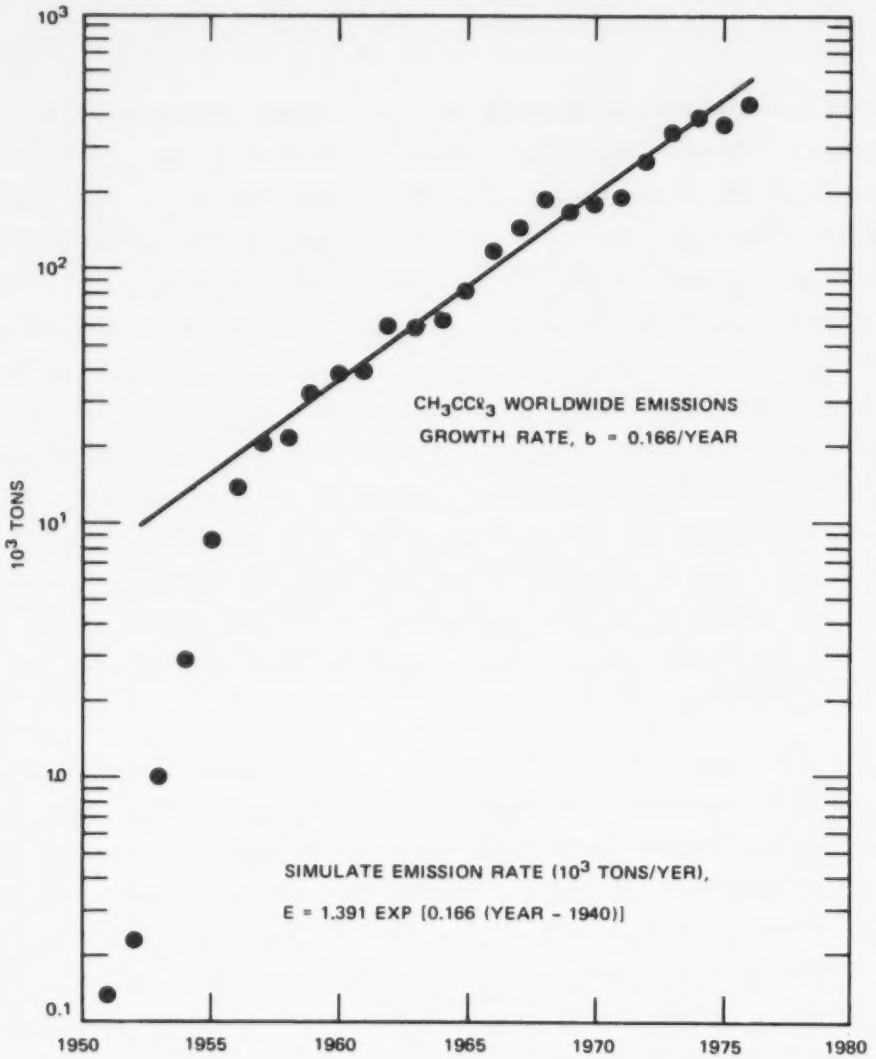


FIGURE 18 GLOBAL EMISSIONS OF METHYL CHLOROFORM

The line in Figure 18 shows an exponential growth rate (b) of 0.166/yr. The emissions up to May 1976 add up to 3.0 million tons of CH_3CCl_3 released. The simulated growth rate (thousand tons/year) can be described as 1.391 exp[0.166 (year-1940)].

If N and S are the cumulative masses and τ_n and τ_s are the residence times (years) of CH_3CCl_3 in the N.H. and the S.H., respectively, then

$$\frac{dN}{dt} = a.\exp(bt) - \frac{N}{\tau_n} - \frac{(N - S)}{\tau_e} \tag{10}$$

$$\frac{dS}{dt} = -\frac{S}{\tau_s} + \frac{(N - S)}{\tau_e} \tag{11}$$

where τ_e is the interhemispheric exchange rate and the function a.exp(bt) represents the time-varying emissions of CH_3CCl_3 in the N.H. The S.H. CH_3CCl_3 emissions are not included in Equation (11) because they are expected to be less than 5% of N.H. emission. Assuming N = S = 0 at t = 0, Equations (10) and (11) can be easily solved to give

$$\frac{N}{S} = \tau_e\left(b + \frac{1}{\tau_e} + \frac{1}{\tau_s}\right) \tag{12}$$

and

$$R = \frac{\text{amount of } CH_3CCl_3 \text{ present}}{\text{cumulative } CH_3CCl_3 \text{ emissions}} = b\,D\left(1 + \frac{N}{S}\right) \tag{13}$$

where $D = 1/[\tau_e(b - \alpha)(b - \beta)]$ and α and β are roots of the equation

$$p^2 + p\left(\frac{2}{\tau_e} + \frac{1}{\tau_s} + \frac{1}{\tau_n}\right) + \frac{1}{\tau_e\tau_n} + \frac{1}{\tau_e\tau_s} + \frac{1}{\tau_n\tau_s} = 0 \quad . \tag{14}$$

The average global residence time τ_a is defined as

$$\tau_a = \frac{[1 + (N/S)]}{\left[\left(1/\tau_s\right) + \left(1/\tau_n\right) \cdot (N/S)\right]} \tag{15}$$

The interhemispheric exchange rate (τ_e) is known from past tracer and meteorological studies. Using a number of tracers, L. Machta from NOAA (personal communication) concludes that the most reliable estimate for τ_e is 14 to 17 months, with 14 months as perhaps the optimum choice. This is also consistent with the fluorocarbon-11 (F11) data of Krey (Committee on Aeronautical and Space Sciences, 1976) taken in 1974, a time when F11 emissions had not been perturbed significantly. From Krey's F11 measurements, N/S = 1.20, and knowing b = 0.14/yr (1969-1974), and τ_s = 30 to 75 years for F11 (Singh, 1977; NAS, 1976), Equation (12) can be used to calculate $\tau_e[= (N/S - 1)/(b + 1/\tau_s)]$ of about 14 to 16

months. Rasmussen's 1976 data show N/S for F11 of 1.13, but it is not possible to calculate τ_e because perturbation in F11 emissions had already taken place. If one considers that these perturbations resulted in a reduction of F11 emissions (lower b), then a value of 14-16 months for τ_e is not in disagreement with this F11 data. For the present calculations, Machta's estimates for τ_e of 14-17 months will be used and 14 months will be considered the optimum τ_e value. While 17 months is probably the accepted upper limit for τ_e, values somewhat lower than 14 months have also been suggested. Newell et al. (1969) has calculated a τ_e of 11 months from exclusively meteorological considerations. This estimate may be low because Hadley cells may return to the original hemisphere without accomplishing complete mixing with the other hemisphere. Additionally, we wish to add that the HO gradient would be even larger for lower values of τ_e. Thus a range of 14-17 months of τ_e is both reliable and conservative.

RESULTS AND DISCUSSION

Given the known values of N/S, R, τ_e, and b, we can use Equations (12), (13), and (15) to calculate τ_s, τ_n, and τ_a. The results are plotted in Figure 19, which clearly shows that τ_a is quite insensitive to all parameters under consideration. Using the lower and upper bounds of measurements (99 and 89 ppt in the N.H., respectively), we calculate an average residence time of eight and 10 years, respectively. We believe eight years is the most reliable estimate of the average global CH_3CCl_3 residence time. Reasonable projections for future release rates of CH_3CCl_3 and a τ_a of eight years lead to a steady state stratospheric O_3 destruction that is about 20% as large as those resulting from continuous release of F11 and F12 at the 1973 rate (private communication of J. McConnel--York University).

As is also clear from Figure 19, for all cases under consideration $\tau_n > \tau_s$. The variation in calculated values of τ_n and τ_s, however, is sensitive to both the N/S ratio and τ_e. For the optimum case of N/S = 1.43, τ_e = 14 months, we get τ_n = 15 years and τ_s = 5 years. Larger

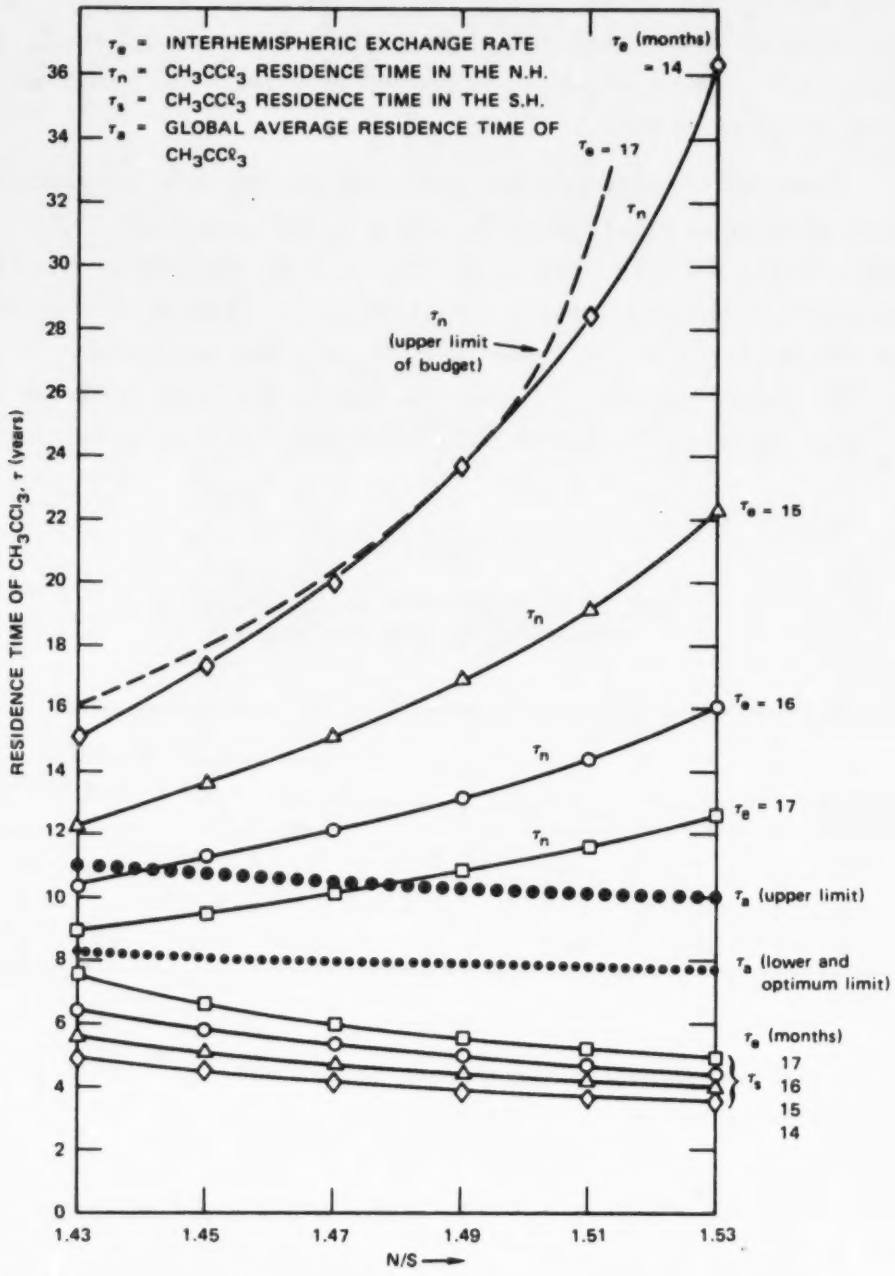


FIGURE 19 METHYL CHLOROFORM RESIDENCE TIMES IN THE NORTHERN AND SOUTHERN HEMISPHERES

N/S ratios result in a much larger difference between τ_n and τ_s. Similarly the upper limits of our tropospheric budget show a much larger difference in τ_n and τ_s, and values of τ_e less than 14 months accomplish the same. The 17-month upper limit of τ_e brings about a closer agreement, in which $\tau_n = 1.3\ \tau_s$. For $\tau_e > 20$ months, which is unrealistic, no clear-cut case of $\tau_n > \tau_s$ can be made.

Thus, while uncertainties remain and the present calculations cannot be considered as final, nevertheless a strong case for $\tau_n > \tau_s$ can be made. Using the rate constant of CH_3CCl_3 + HO reaction at the weighted average tropospheric temperature of 265°K ($k = 9.64 \times 10^{-15}$ ml/mol/s), we can calculate the HO burden from CH_3CCl_3 residence times. For the optimum conditions (N/S = 1.43), the results are shown in Table 11. Thus we find that a global average HO ($\overline{HO}$) concentration of about 4×10^5 HO/ml

Table 11

RESIDENCE TIMES OF CH_3CCl_3 AND THE HO ABUNDANCE, IN THE N.H. AND S.H.

				$\overline{HO}$/ml $\times 10^5$		
(months)	(years)	(years)	(years)	N.H.	S.H.	Av.$\left(\frac{\text{N.H. + S.H.}}{2}\right)$
14	15.0	5.0	8.3	2.1	6.3	4.2
15	12.2	5.6	8.3	2.6	5.6	4.1
16	10.4	6.4	8.3	3.1	5.0	4.1

is consistent with the observational data. Table 11 also shows that for reasonable estimates of τ_e (14-16 months),

$$\frac{(\overline{HO})_{N.H.} + (\overline{HO})_{S.H.}}{2} = (\overline{HO}) = 4.1 \times 10^5 \text{ HO/ml} \qquad (16)$$

$$\frac{(\overline{HO})_{S.H.}}{(\overline{HO})_{N.H.}} = 1.6 \text{ to } 3 \qquad (17)$$

Although some differences in the N.H. and S.H. levels of HO are to be expected because of natural differences in water vapor, ozone, and particulate concentrations, a much larger difference can be attributed, at least in part, to CO (a principal sink for HO), whose levels are three times higher in the N.H. when compared with the S.H. (Seiler, 1974). The HO asymmetries based on an analysis of the atmospheric abundance of CH_3CCl_3 are also in agreement with the present CH_4-CO-H_2 balance in the troposphere (Crutzen and Fishman, 1977). If the additional CO in the N.H. is because of man-made sources predominantly, as the current data seem to suggest, continued release of CO has and will further reduce the HO levels, thereby depleting the scavenging ability of the atmosphere. A switch to fossil fuels in coming years is likely to cause more severe depletions in the HO abundance. These HO losses will not only allow a larger stratospheric input of anthropogenic halocarbons and hydrocarbons but may already have altered the stratospheric chemistry by permitting increased intrusion of natural tropospheric species such as CH_4 and CH_3Cl. In addition, continuous exponential growth of CH_3CCl_3 at its present rates is likely to be a cause of concern because of potential effects on the stratospheric ozone. The effect may be further escalated in the future as more and more nations substitute CH_3CCl_3 to replace declining usage of C_2HCl_3 and to some extent C_2Cl_4 (for toxicity and health reasons), thereby causing extraordinary increases in CH_3CCl_3 emissions.

HALOCARBONS AND N_2O STANDARDS INTERCOMPARISON

Because halocarbons are relatively new pollutants present at very low concentrations, the generation of primary standards is a difficult and tedious task. At the same time, the needs are such that an extremely high degree of accuracy is required. There are no agreed-upon sources of primary standards. To test the uncertainties in measurements, identical samples of air of unknown composition were analyzed by SRI and Washington State University (WSU) independently. The results of this intercomparison are shown in Table 12 and indicate reasonable agreement.

Table 12

ANALYSIS AND INTERCOMPARISON OF AN IDENTICAL AIR SAMPLE BY SRI AND WSU

	Concentration (ppt)	
Compound	SRI	WSU
N_2O	312×10^3	329×10^3
F12	224	250
F11	124	150
CH_3CCl_3	106	104
CCl_4	122	150

FUTURE PLANS

A great deal of field data was collected during Phase I of the second year research effort. While the data has been processed, the analysis is by no means complete. Additional analysis will appear in subsequent reports and publications. In the immediate future, however, the emphasis is shifting to a global monitoring program for the halocarbon and hydrocarbon trace constituents. Four trips into the southern hemisphere are planned. In three of the trips, samples will be collected at several selected locations between 60°N and 60°S and analyzed at SRI. Specially treated stainless steel and glass containers of one-liter size will be used to collect air at 25 psi. Clean metal bellows pumps will be used for pressurization. The fourth trip to the southern hemisphere will be an oceanographic cruise from San Francisco to New Zeland. Air and ocean water analysis will be conducted in situ during this cruise. Limited air samples from the South Pole will be complemented with these data.

The main objective of the Phase II effort of the second year research will be to understand interhemispheric variations and to collect more extensive southern hemispheric data.

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LIST OF PUBLICATIONS

The following is a list of papers accepted for publication based on the research efforts of the first year and portions of the second year:

- "Atmospheric Carbon Tetrachloride: Another Man-Made Pollutant," Science, Vol. 192, p. 1231 (1976).
- "Phosgene in the Ambient Air," Nature, Vol. 264, p. 428 (1976).
- "Generation of Accurate Halocarbon Primary Standards from Permeation Tubes," Env. Sci. and Tech., Vol. 11, p. 511 (1977).
- "Distribution, Sources and Sinks of Atmospheric Halogenated Compounds," J. Air Pollution Control Assoc., Vol. 27, p. 332 (1977).
- "Atmospheric Halocarbons: Evidence in Favor of Reduced Average Hydroxyl Radical Concentrations in the Troposphere," Geophys. Res. Letters, Vol. 4, p. 101 (1977).
- "Urban-Nonurban Relationships of Halocarbons, SF_6, N_2O and Other Atmospheric Trace Constituents," Atm. Env., in press (September 1977).
- "Preliminary Estimation of Average Tropospheric HO Concentrations in the Northern and Southern Hemispheres," Geophys. Res. Letters, in press (1977).